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Review

Composite reverse osmosis and nanofiltration membranes

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a phase separation medium. In early studies at North Star Research Institute, beneficial additives at levels of up to 20% of the N,N-dimethylformamide solvent included the methyl, ethyl and butyl cellosolves, acetone, tetrahydrofuran, diacetone alcohol, ethyl lactate and t-amyl alcohol [10]. More recently, Hou et al. [19] examined an extensive series of organic additives and their mechanism of action in polysulfone casting solutions. Methyl cellosolve (2-methoxyethanol) has been often used in commercially cast polysulfone supports as a nonsolvent additive.

Polymers have also been examined as additives to polysulfone casting solutions. In particular, polyvinyl pyrrolidinone (PVP) was found to be compatible with polysulfone at all proportions, and was used by Cabasso et al. [20] as a viscosity promoting agent in the extrusion of hollow microporous fibers. Being water-soluble, it was mostly extracted in the water-quenching and rinsing steps. PVP has also been used for the same purpose with polyethersulfone hollow fiber extrusions [21]. Polymers incompatible with polysulfone can be mixed into the casting solution, if held to low levels (2 to 5% of the polysulfone on a weight basis), but must be thoroughly mixed before casting [10].

High viscosity solutions of polysulfone can also be made using 1:1 Lewis acid:base complexes as solvents, as recently discovered by Kesting and co-workers [22,23]. Examples of such solvent complexes were propionic acid with N-methylpyrrolidinone or N,N-dimethylacetamide, and acetic acid with N-methylpyrrolidinone. Hollow fibers free of macrovoids were spun from high viscosity, high total solids solutions of this type. The Lewis acid:base complexes disassociated upon contact with water and were easily extracted. The primary use of this approach was targeted toward gas separation membranes rather than reverse osmosis membranes.

Polysulfone is not without its drawbacks as a composite membrane support. One difficulty is its hydrophobic character, which can cause problems with low pressure membranes, especially if such membranes are allowed to partially dry out after usage. A second difficulty is the solvent sensitivity of polysulfone, which eliminates most solvent-based coating solutions for depositing a polymer barrier layer. This solvent sensitivity also eliminates the use of polysulfone-supported membranes in the processing of most solvent-based feed solutions.

Polyethersulfone has been used commercially as an alternative support film for polymeric composite membranes. Other polymers mentioned at one time or another in the membrane literature as porous supports include cellulose mixed esters, polyimides, polyphenylene oxides, poly(styrene-co-acrylonitrile), polyacrylonitrile, polyvinyl chloride and poly(butylene terephthalate). In the case of dynamic membranes, ceramic, carbon and stainless steel sintered porous supports have all been used as the base layers.

Interfacially polymerized composite membranes

The advent of microporous polysulfone as a support layer for composite membranes enabled one to use barrier-forming solutions that were highly acidic or alkaline. This was especially beneficial in the area of interfacial polyamide membranes where the support is customarily coated with an alkaline amine solution, particularly when caustic is used as an acid acceptor. Microporous cellulose ester supports would not survive such an exposure intact. Since then, the field of composite reverse osmosis membranes has overwhelmingly moved in the direction of interfacially synthesized membranes, dominated by polyamide compositions. This represents perhaps the only significant commercial application of interfacial polymerization technology to come forth from the vast amount of work on the technique during the 1940s and 1950s.

The subject of interfacial polymerization was treated extensively in the book *Condensation Polymers: By Interfacial and Solution Methods*, by P.W. Morgan [24]. The concept of interfacially formed membranes was only briefly addressed, however. Interfacially formed membranes were found to be leaky to small molecules such as salts and small dyes. This observation was confirmed in unpublished work by Cadotte during the late 1960s and in work by Lonsdale and co-workers [25]. Scala and co-workers [26] had apparently achieved salt rejections as high as 85% in interfacially polymerized polyamide membranes, but only by a technique that generated thick barrier layers characterized by very low water flux and essentially no commercial utility. Today, high flux/high rejection membranes can now be routinely prepared. The key advance appears to be, in retrospect, the simultaneous crosslinking of the nascent polymer film as it forms at an interface.

In Chapter 2 of Morgan's book, evidence is summarized leading to the conclusion that interfacial polymerization occurs in the organic phase. For instance, in order for 1,6-hexanediamine contained in water to react with sebacoyl chloride contained in hexane, the hexanediamine must diffuse across the water–hexane interface to make reactive contact with the sebacoyl chloride. Reaction does not take place in the water phase, because a highly unfavorable partition coefficient for sebacoyl chloride limits its availability in the aqueous phase. For film thickness to build up, amine must continually cross the water–hexane interface, diffuse through the polyamide layer already formed, then come into contact with acyl halide on the organic solvent side of the polyamide layer. Thus, new polymer forms on the organic solvent side of polyamide film.

This has been demonstrated in a visually graphic way by depositing colored powder on the surface of the film facing the organic phase (see Fig. 4). The powder becomes embedded inside the film as interfacial polymerization continues. However, if colored powder is deposited on the aqueous phase side of the film (using an organic solvent denser than water), the powder does not become embedded in the resulting film.

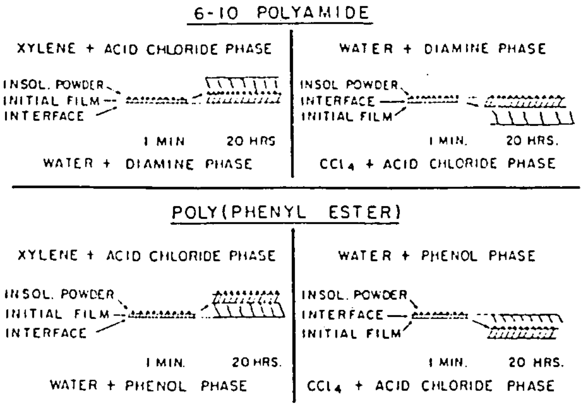


Fig. 4. Illustration of the locus of polymer formation by means of colored powders during interfacial polymerization [24].

The composition and morphology of the interfacially formed polymer film will be dependent on several variables, including:

(a) concentration of reactants;

(b) partition coefficients of the reactants;

(c) reactivity ratios where blends of reactants are employed;

(d) solubility of nascent polymer in the solvent phase as it is formed;

(e) the overall kinetics and diffusion rates of the reactants;

(f) presence of by-products (such as hydrogen chloride in the case of reaction of amine with an acyl chloride);

(g) hydrolysis or other potentially competitive by-reactions;

(h) crosslinking reactions; and

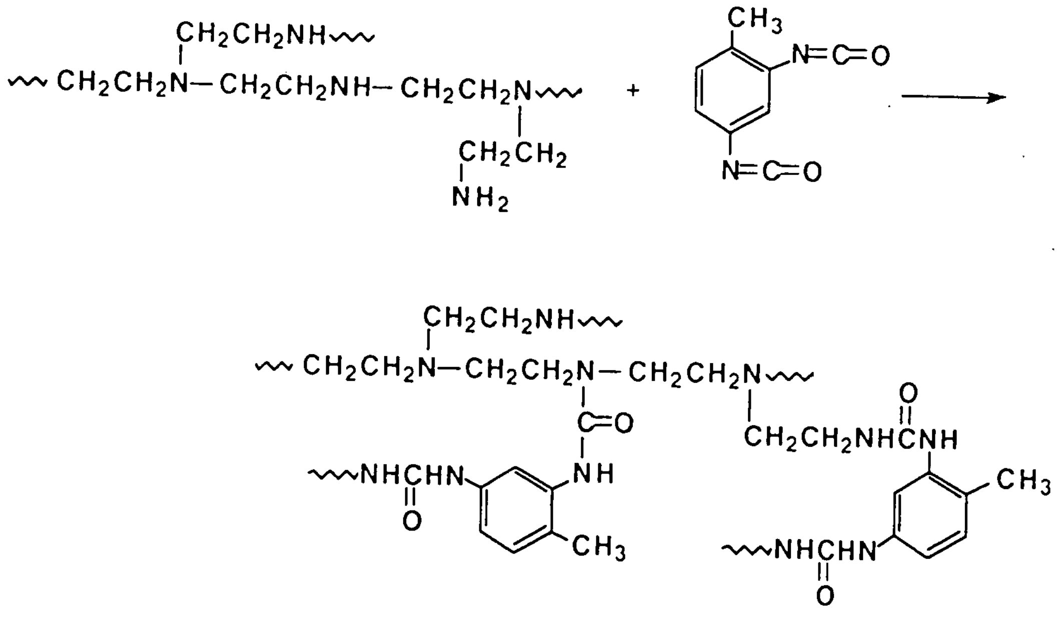
(i) post-reactions or treatments of the resulting interfacial films.

The first five of these factors must be considered to adequately explain membrane formation behavior and subsequent properties. The latter four factors should also be considered for their effect on the membrane's performance properties. Cadotte and co-workers [27] dealt with some of these factors in a paper on interfacial synthesis of reverse osmosis membranes. Also, in a paper presented at the 1987 ICOM meeting in Tokyo, Sundet [28] described to some degree the mechanism of interfacial polyamide formation, and concluded that an interfacially formed polyamide layer would be asymmetric and highly functional (i.e. many terminal groups). Overall, however, very little has been published in this regard with respect to thin film composite membranes.

The NS-100 membrane: polyethylenimine-based composites

In 1969–1970, Cadotte determined in unpublished exploratory work that high rejection reverse osmosis membranes could be made from polyethylenimine using an interfacial reaction technique. This finding resulted in funding by the Office of Saline Water of a research program at North Star Research Institute, from which the NS-100 membrane came forth [29–31].

The polyethylenimine used in Cadotte's work was a branched, essentially globular polymer made by a ring-opening polymerization of aziridine and having approximately a 3:4:3 ratio of primary:secondary:tertiary amine groups. Polyethylenimine molecular weights of 10,000 to 60,000 provided satisfactory membranes. A water-saturated microporous polysulfone sheet, sitting in a petri-dish, was immersed in an aqueous solution of polyethylenimine (typically a 0.67% solution in deionized water) for two minutes, then positioned vertically to drain for two minutes. It was then immersed in a hexane solution containing 0.1% toluene diisocyanate for a period of 30 to 60 seconds. The hexane solution was drained off, and the coated substrate was heat-cured in an air-circulating oven at about 110°C for 15 min. The chemistry of the reaction is illustrated in Scheme 1.



Scheme 1.

The reaction of toluene diisocyanate with polyethylenimine generated a polyurea, which provided the permselective characteristics. Some indication of biuret formation at the 110°C curing condition was also detected in infrared spectroscopic studies [32]. This membrane gave better than 99% salt rejection, with a flux of 18 gfd, when tested at 1500 psig on 3.5% synthetic seawater.

Later it was found that an equally useful membrane was obtained if isophthaloyl chloride was used instead of toluene diisocyanate, thereby generating a polyamide [33]. The polyamide version showed a somewhat higher flux than the polyurea version, but the polyurea showed a somewhat higher level of solute rejections and exhibited better durability in long term field tests.

The NS-100 membrane was a major technological milestone in several respects. It was the first successful example of a noncellulosic composite reverse osmosis membrane. It was the first example of an interfacially formed membrane having high rejections of small salts. Furthermore, its rejection levels towards small organic molecules greatly exceeded rejection levels of other known reverse osmosis membranes at the time. It exhibited single-pass seawater desalination characteristics at water fluxes greatly exceeding fluxes for comparable cellulose acetate membranes. It was capable of being operated at temperatures in excess of 35°C, which was a temperature ceiling for commercial asymmetric membranes. And it possessed superior chemical resistance to acids and alkalies. Its one significant shortcoming was an almost total lack of resistance to halogen-based disinfectants, particularly hypochlorous acid and hypochlorite ion.

Scanning electron microscopy on the NS-100 membrane showed it to have a smooth, featureless surface [1,27]. Also, studies on the membrane indicated that the high temperature cure step was a necessary step for membrane stability [29]. Otherwise, poor salt rejection was observed under seawater test conditions. Infrared spectra indicated the polyethylenimine layer in the membrane was not completely consumed in the reaction with the organic phase reactant, but was insolubilized by the heat treatment [32]. Experiments also showed that a polyethylenimine coating on the microporous polysulfone support could be insolubilized by heat alone, to generate a loose barrier layer having high flux and low salt rejection.

These facts were all consistent with a probability that reaction of the polyethylenimine with toluene diisocyanate or isophthaloyl chloride did not take place in the organic phase, in contrast to the case for monomeric amine reactants outlined by Morgan. The unfavorable partition coefficient for the bulky polyethylenimine molecule inhibited its movement into the organic phase. Furthermore, the polymeric lattice formed by reaction of the polymeric amine with the crosslinking reactant would act as a barrier to diffusion of the polymeric amine to the organic phase. Therefore, the organic phase reactant necessarily had to enter the aqueous phase to react with this polymeric polyamine. Since this was also unfavorable, the depth of reaction was limited, producing an extremely thin, dense barrier layer. Hence, stabilization of the barrier layer by the heat-curing of the underlying unreacted polyethylenimine was necessary. This theory also fit with the probability that isophthaloyl chloride was less likely to penetrate to the same depth as toluene diisocyanate into the aqueous polyethylenimine layer, consequently giving rise to a thinner dense layer characterized by a higher water flux.

A later study by Bartels [34] came to a different conclusion. Polyethylenimine–toluene diisocyanate composite membranes were formed under substantially the same conditions as Cadotte. The membranes were then analyzed with a variety of techniques. In particular, ATR-IR analyses indicated that the polyurea film was roughly 0.6 μm thick, which was about the same thickness as found for the barrier layer by SEM and TEM techniques. It was concluded therefrom that the entire film thickness was probably composed of the polyurea product. Also shown in this study was the presence of unreacted secondary amine groups in the coating, but no primary amine groups. This work was an outgrowth of an interest in polyethylenimine-based composite membranes for removal of water from alcohols and ketones by pervaporation [35].

Mysels and Wrasidlo [36] studied interfacial films of polyethylenimine reacted with toluene diisocyanate by a method of extruding a drop of aqueous polyethylenimine solution underneath the surface of a hexane solution of the diisocyanate. From surface tension forces, they determined that the barrier layer had a strength of about 100 dynes/cm. This strength was sufficient to withstand hydraulic pressures of up to 100 atmospheres (about 1500 psig) when supported on microporous polysulfone supports having pore sizes of 400 Å or less, but not for larger pores. This technique may have application in determining the true thickness of the ultrathin polyurea barrier layer separate from any contribution of heat-crosslinked polyethylenimine.

Chen and Chan [37] studied the mechanism of NS-100 formation, including use of radio-labeled ethanolamine to measure residual levels of unreacted isocyanate groups in the barrier layer. They concluded that the 110°C post-cure enhanced salt rejection by promoting additional crosslink formation via reactions of the residual isocyanate groups.

Optimization studies were carried out on NS-100 by Fang and Chian [38]. They followed a statistically designed set of parameters to obtain a membrane having 10.30 ± 1.95 gfd and 99.30 ± 0.18% salt rejection in contact with a 5000 ppm NaCl solution at 600 psig. They also evaluated the membrane for several applications requiring removal of organic compounds and pesticides [39]. Sudak and co-workers [40] used a statistically designed format to develop a version (MSI-400) optimized for low pressure operation on brackish water. They achieved a membrane that gave 20 gfd flux and 97% salt rejection in contact with a 5000 ppm NaCl solution at 250 psig. They also achieved a seawater version that gave 17 gfd and 99% salt rejection on 3.5% NaCl solution, tested at 800 psig and 24°C.

Yang and Dickson [41] prepared a series of polyethylenimine-based polyamide composite membranes, interfacially reacting polyethylenimine on a polysulfone support with blends of acyl halides. They measured the transport characteristics of a membrane made with an optimal ratio of 0.1:0.4 wt.% terephthaloyl chloride:isophthaloyl chloride in hexane and satisfactorily modeled the transport characteristics of this membrane using a finely-porous transport model, a modification of the Kimura–Sourirajan surface force–porous flow model.

The polyurea barrier layer was known to be severely damaged by as little as one day's storage in chlorinated municipal tapwater. Oxidative cleavage of the polyethylenimine backbone by chlorine (hypochlorous acid, hypochlorite ion) via attack on the nitrogen centers, especially the secondary amine sites, was postulated. The susceptibility of the NS-100 membrane to chlorine attack could be modified somewhat by cyanoethylation of the primary amine groups in polyethylenimine, according to Wrasidlo [42]. The resulting membrane was claimed to be chlorine-resistant, though this was probably not true. Claims of chlorine resistance appear to be commonly exaggerated in patent applications on composite reverse osmosis membranes.

Rozelle and co-workers [43] showed the promise of the NS-100 membrane in the treatment of alkaline cyanide rinse baths for electroplating operations. Petersen and Cobian [44] subsequently prepared NS-100 tubular membranes for cyanide wastewater treatment. Rejections of 95% were obtained on cyanide ion in reverse osmosis treatment of pH 12 zinc and copper cyanide baths by the NS-100 membranes.

Baker and Barss [45] have patented a hollow fiber composite membrane where an NS-100 membrane layer is deposited on the inside walls of the fibers. Superior resistance to fouling by wastewaters was obtained with such a membrane structure compared to other forms of membrane modules.

The PA-300 and RC-100 membranes: polyepiamine-based composites

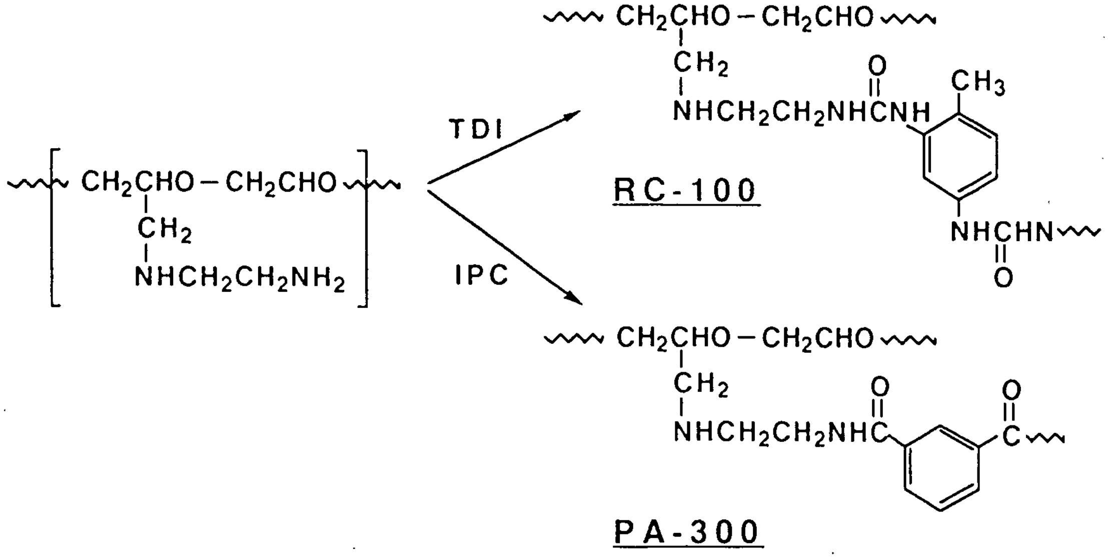
The success with the NS-100 membrane set the direction for several years in the area of interfacially formed composite membranes. A wide variety of aminated *polymers* were evaluated by various groups, all following the thesis that the amine should be in a polymeric form for good results. One such polymeric amine is widely known to have culminated in a commercial product: polyepiamine [46,47]. This polymer gave reverse osmosis membranes with high salt rejections and superior permeate fluxes compared to polyethylenimine. Interfacial membranes made with isophthaloyl chloride were designated as PA-300, and corresponding products made with toluene diisocyanate were designated as RC-100, and were developed into commercial products by Riley and co-workers [48]. These membranes were originally designed for seawater desalination. A brackish water version of the PA-300 membrane, designated as LP-300, was also developed [49]. The membrane product currently designated as TFC® by UOP Fluid Systems is believed, however, to correspond primarily to the RC-100 version.

Polyepiamine is the reaction product of polyepichlorohydrin with 1,2-ethanediamine, prepared in such a way as to minimize branching and crosslinking. Also known as polyetheramine, polyepiamine was originally developed commercially as a cationic flocculant for wastewater treatment. Because of shelf stability problems, polyepiamine was withdrawn from commercial production, and now must be synthesized by the membrane fabricator. The idealized chemistry of the PA-300 and RC-100 membranes is illustrated in Scheme 2.

Both primary and secondary amine sites exist in the polyepiamine, and both would be expected to participate in crosslinking reactions with the diisocyanate or the diacyl halide.

The PA-300 membrane exhibited fluxes of 20–25 gfd and salt rejections in excess of 99.4% in contact with 3.5% aqueous sodium chloride solution at 1000 psig feedwater pressure. Optimum feedwater pH at which these results were obtainable was at 5.0 to 6.0; salt rejections fell off modestly at higher pH levels. A brackish water version of the membrane showed 20 gfd flux and 98% rejection in contact with a 5,530 ppm NaCl solution at 400 psig. An even lower pressure version of the PA-300 membrane, designated as LP-300, was developed later. This version generated up to 24 gfd flux at 98.5% salt rejection when tested on a simulated brackish agricultural drainage water at 200 psig. To obtain high fluxes, it was important to control molecular weight such that the polyepiamine did not fill the pores of the porous support. Otherwise, water flux would be impeded by plugs of crosslinked polymer in the polysulfone pores.

Pusch [50] has published a study of the transport of various alkali salts through asymmetric cellulose acetate membranes in comparison with a strong cation exchange membrane. The study also included comparative data for the RC-100 composite poly(etherurea) membrane and for an asymmetric aromatic polyamide membrane. Normalized salt permeabilities



Scheme 2.

of sodium salts, calculated from plots of reciprocal flux versus reciprocal rejection, increased in the order $Cl^- < NO_3^- < Br^- < I^-$ for all the reverse osmosis membranes, the opposite order being seen for the cation exchange membrane. In the case of the alkali nitrate salts, normalized salt permeabilities for the RC-100 membrane increased in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, which paralleled the order observed for the cation exchange membrane. This trend was less regular for the other two membranes. In the case of the alkali chloride salts, the cation exchange membrane showed normalized salt permeabilities in the same order as for the nitrate salts, but for all three reverse osmosis membranes the order generally trended in the reverse direction and was irregular.

The first major installation of a composite reverse osmosis membrane in the world, i.e. the 3.2 million gallon per day seawater desalination plant at Jeddah, Saudi Arabia, utilized the PA-300 membrane in the form of spiral-wound elements [51,52]. Because of the high salinity of the seawater feed, this was a two-pass plant, i.e. part of the membrane permeate was passed through a second membrane stage to reduce the final permeate salt content to required levels. The PA-300 membrane apparently has not shown sufficient stability for long term seawater service, and it is believed that much of the PA-300 membrane at Jeddah was eventually replaced with the RC-100 membrane version. However, early PA-300 replacements occurred for a non-membrane-related problem with one of the spiral element construction materials, rather than for a membrane performance issue. The TFC membrane has also been used in single-stage seawater desalination installations.

The TFC membrane is claimed to be less subject to microbiological fouling than other reverse osmosis membranes [53], based on a study of bioattachment rates by micro-organisms cultured from Orange County Water District's Water Factor 21 installation [54,55]. A TFC installation (Umm Lujj II) in Saudi Arabia was successfully operated for two years on nonchlorinated seawater, using only copper sulfate dosing for control of algae plankton growth [53]. Biofouling by microorganisms, if present, was not evident in terms of flux decline. Similar use of copper sulfate dosing with TFC membranes was employed at seawater desalting installations in Jeddah (Saudi Arabia), Rosarito Beach (Mexico) and Ras Tajura (Libya).

The polyepiamine-based and the polyethylenimine-based membranes share a common characteristic of having a net cationic charge due to a significant residual content of unreacted amine. One way in which this is evident is the affinity of the NS-100/PA-300/RC-100 membranes for anionic surfactants. Absorption of anionic surfactants by these membranes causes a loss of flux due to the effects of the hydrophobic portions of the surfactants. Applications such as laundry wastewater treatment are ruled out by this behavior. On the other hand, disinfection and preservation of such membranes from bio-growth by means of quaternary surfactants can be practiced, and is done so for TFC membrane spiral-wound elements supplied to the U.S. military.

One version of the TFC spiral-wound element has been developed for high temperature applications, such as the concentration of sugar beet thin juice. Stable membrane fluxes of 10 to 15 gfd at conditions of 80°C and 400 psi net driving pressure were achieved [56,57]. The membrane was described as approvable for food contact. The U.S. Food and Drug Administration (FDA) has approved a polyepiamine derivative, the polymer composed of epichlorohydrin–ethylenediamine–1,2-dichloroethane, for food contact [58].

Interfacial membranes based on other polymeric polyamines

Following the basic approach of the NS-100 membrane methodology, numerous other polymeric amine compositions have been synthesized and evaluated in interfacially formed composite membranes. Many of these are described only in patents and laid-open patent applications. A few commercial products have been developed that appear to fit into this category based on their performance characteristics or on correlative patent activity.

Among commercial membranes of this type are the Nitto Denko NTR-7100 series: NTR-7197 and NTR-7199 membranes [59]. The NTR-7199 membrane is known to contain a polyurea barrier layer [60], and this is believed to be so for the NTR-7197 membrane as well, the only difference being salt rejection. The full composition of the NTR-7199 membrane barrier layer has not been published. A graph of salt rejection versus flux for this membrane compared to others available circa 1983 has been published by Kamiyama and co-workers [59], and is shown in Fig. 5. The performance envelope of the membrane almost perfectly matches that of the PA-300 membrane. The NTR-7199 membrane has been studied for

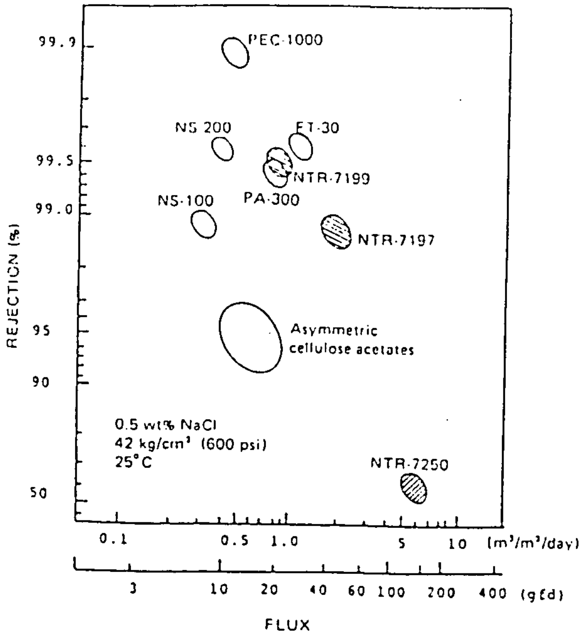


Fig. 5. Plot of rejection versus flux for the Nitto Denko NTR-7199 membrane relative to other reverse osmosis membranes [59].

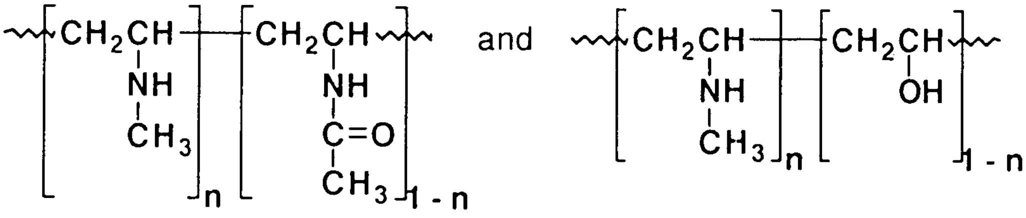
concentration of alcohol–water solutions [61].

Another membrane, recently introduced in tubular form, that appears to contain an interfacially crosslinked polymeric polyamine is the Wafilin WFC-X006 composite membrane [62]. The membrane contains a crosslinked polyamide having some residual secondary amine groups therein. A membrane of this nature has been described by Buys and co-workers [63], wherein two types of vinyl amine copolymers, shown below, were prepared and interfacially crosslinked with polyacyl halides (see Scheme 3).

Sodium chloride rejections exceeding 99% were obtained using polyvinylamines, possibly blended with monomeric or oligomeric amines. A corresponding patent application by Wafilin [64] describes coating a tubular polysulfone support with an aqueous solution containing 0.5% poly(N-vinylamine-co-N-vinyl-N-methylacetamide) and 1.0% of a monomeric diamine, then interfacially reacting the coating with a hexane solution of 1.8% 1,2,5-thiadiazole-3,5-dicarbonyl chloride blended with 0.2% trimesoyl chloride.

A patent awarded to Kurihara et al. [65] of Toray Industries described the preparation and use of several polyether-amines in composite interfacial membranes. For example, poly-epichlorohydrin was converted to polyepiiodohydrin with sodium iodide, and the iodo form was then reacted with selected amines to generate polyethers having pendant amine groups. Preferred examples of such amines appeared to be 3-methylamino-hexahydroazepine, 3-amino-hexahydroazepine, and 4-aminomethyl-piperidine (referred to in the patent as a 4-amino-methyl-piperizine). They also reacted the polyepiiodohydrin with sodium azide to produce a polyazido compound, and reduced the azide to a primary amine function to generate the simplest example of a polyepiamine: poly(1-aminomethyl-1,2-ethylene oxide). These polymers were used alone or in combination with monomeric diamines in interfacial polymerizations with diacyl halides, typically with isophthaloyl chloride in hexane. Best results were obtained when a substantial portion of the amine reactants was composed of monomeric amine. In seawater desalination tests using a 3.5% NaCl solution as a simulated seawater feed, salt rejections of as high as 99.5% were achieved at fluxes of 8 to 9 gfd (800 psig test pressure, 25°C).

Uemura and Kurihara [66] further described the approach of using amine monomer/polymer combinations in interfacial composite membrane preparation. Figure 6 shows the three layer barrier zone theorized to have resulted from this approach. The middle layer would consist of thin layer of polymeric polyamine and monomeric amine, both crosslinked with the diacyl reactant. During further interfacial reaction, monomeric amine diffuses through this initially formed layer, reacts with diacyl halide, and deposits a layer devoid of the polymeric polyamine on the membrane surface. This is claimed to result in higher salt rejections than the case of the polymeric amine without monomer amine. Underneath these two



$$\sim[CH_2CH(NHCH_3)]_n[CH_2CH(NHC(=O)CH_3)]_{1-n}\sim \quad \text{and} \quad \sim[CH_2CH(NHCH_3)]_n[CH_2CH(OH)]_{1-n}\sim$$

Scheme 3.

present, was not evident in terms of flux decline. Similar use of copper sulfate dosing with TFC membranes was employed at seawater desalting installations in Jeddah (Saudi Arabia), Rosarito Beach (Mexico) and Ras Tajura (Libya).

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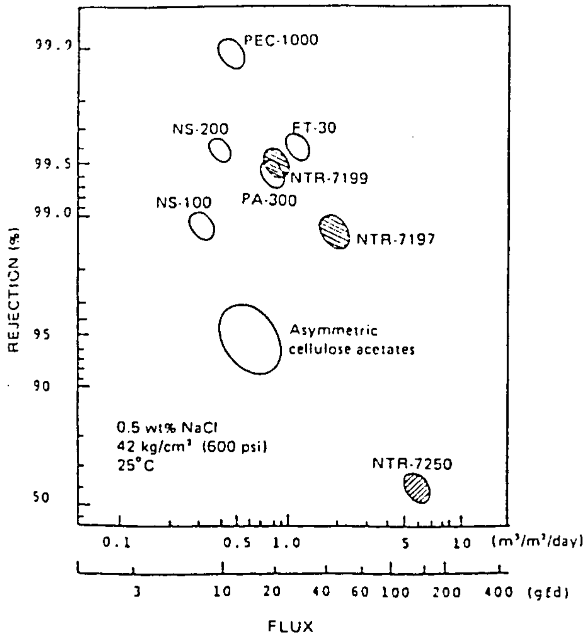

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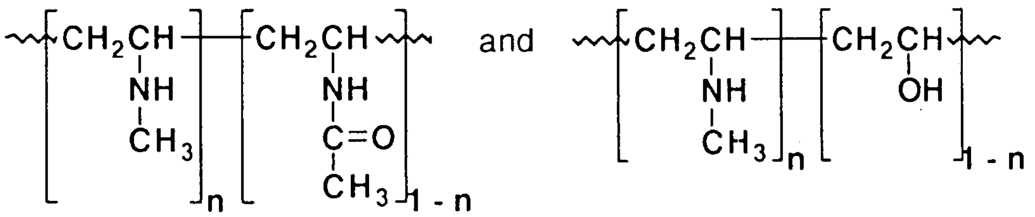
concentration of alcohol–water solutions [61].

Another membrane, recently introduced in tubular form, that appears to contain an interfacially crosslinked polymeric polyamine is the Wafilin WFC-X006 composite membrane [62]. The membrane contains a crosslinked polyamide having some residual secondary amine groups therein. A membrane of this nature has been described by Buys and co-workers [63], wherein two types of vinyl amine copolymers, shown below, were prepared and interfacially crosslinked with polyacyl halides (see Scheme 3).

Sodium chloride rejections exceeding 99% were obtained using polyvinylamines, possibly blended with monomeric or oligomeric amines. A corresponding patent application by Wafilin [64] describes coating a tubular polysulfone support with an aqueous solution containing 0.5% poly(N-vinylamine-co-N-vinyl-N-methylacetamide) and 1.0% of a monomeric diamine, then interfacially reacting the coating with a hexane solution of 1.8% 1,2,5-thiadiazole-3,5-dicarbonyl chloride blended with 0.2% trimesoyl chloride.

A patent awarded to Kurihara et al. [65] of Toray Industries described the preparation and use of several polyether-amines in composite interfacial membranes. For example, poly-epichlorohydrin was converted to polyepiiodohydrin with sodium iodide, and the iodo form was then reacted with selected amines to generate polyethers having pendant amine groups. Preferred examples of such amines appeared to be 3-methylamino-hexahydroazepine, 3-amino-hexahydroazepine, and 4-aminomethyl-piperidine (referred to in the patent as a 4-aminomethyl-piperizine). They also reacted the polyepiiodohydrin with sodium azide to produce a polyazido compound, and reduced the azide to a primary amine function to generate the simplest example of a polyepiamine: poly(1-aminomethyl-1,2-ethylene oxide). These polymers were used alone or in combination with monomeric diamines in interfacial polymerizations with diacyl halides, typically with isophthaloyl chloride in hexane. Best results were obtained when a substantial portion of the amine reactants was composed of monomeric amine. In seawater desalination tests using a 3.5% NaCl solution as a simulated seawater feed, salt rejections of as high as 99.5% were achieved at fluxes of 8 to 9 gfd (800 psig test pressure, 25°C).

Uemura and Kurihara [66] further described the approach of using amine monomer/polymer combinations in interfacial composite membrane preparation. Figure 6 shows the three layer barrier zone theorized to have resulted from this approach. The middle layer would consist of thin layer of polymeric polyamine and monomeric amine, both crosslinked with the diacyl reactant. During further interfacial reaction, monomeric amine diffuses through this initially formed layer, reacts with diacyl halide, and deposits a layer devoid of the polymeric polyamine on the membrane surface. This is claimed to result in higher salt rejections than the case of the polymeric amine without monomer amine. Underneath these two



$\sim\!\left[CH_2CH(NHCH_3)\right]_n\left[CH_2CH(NHC(=O)CH_3)\right]_{1-n}\!\sim$ and $\sim\!\left[CH_2CH(NHCH_3)\right]_n\left[CH_2CH(OH)\right]_{1-n}\!\sim$

Scheme 3.

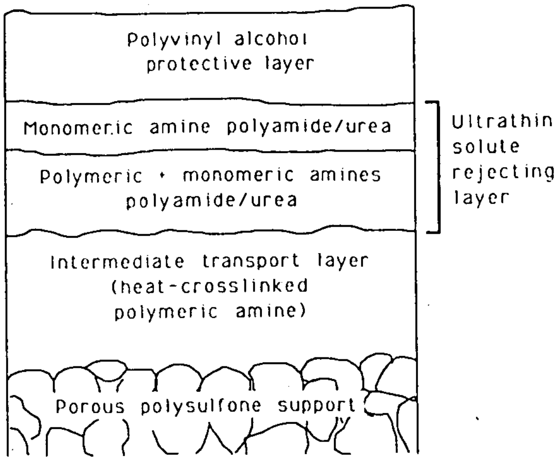

Polyvinyl alcohol protective layer
Monomeric amine polyamide/urea
Polymeric + monomeric amines polyamide/urea
Ultrathin solute rejecting layer
Intermediate transport layer (heat-crosslinked polymeric amine)
Porous polysulfone support

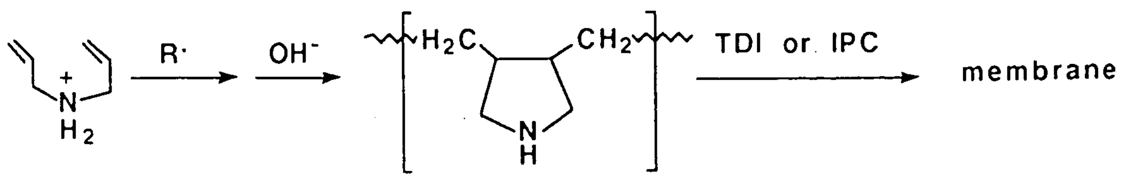
Fig. 6. Schematic diagram of a three layer barrier film formed from interfacial polymerization of a blend of monomeric and polymeric polyamines with a crosslinking reagent [66].

layers is a residual layer of unreacted polymeric polyamine, which is crosslinked by a heat-cure step.

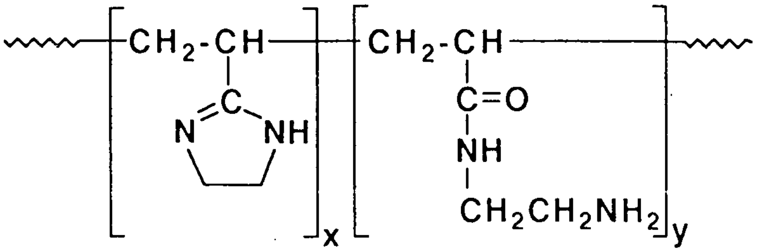
Another series of polymers based on poly(diallyl amine) are described in a patent awarded to Kawaguchi and co-workers [67] of Teijin. Homopolymers of diallyl amine, copolymers of this amine with sulfur dioxide, and terpolymers with vinyl compounds were synthesized, then interfacially reacted with crosslinking agents such as diisocyanates, diacyl halides and triacyl halides. The chemistry of the poly(diallyl amine) approach is shown below. The patent description refers to the diallyl amine polymers as polypiperidines, but academic publications by others have since shown that diallyl amines preferably polymerize to produce polypyrrolidines (see Scheme 4).

The amine groups in diallyl amine polymers and copolymers are all secondary amines. This was of particular interest because resulting polyamides could be expected to exhibit greatly improved chlorine resistance compared to NS-100, PA-300 and RC-100. Since no amidic hydrogen would be present in the poly(diallyl amine) polyamides, no site for initiation of chlorine attack was supposedly present. Chlorine-resistance tests were conducted at 600 psig with a feedwater containing 0.5% NaCl and 5 ppm active chlorine (pH 6.0 to 6.5 for 40 to 80 hr on resulting polyamide compositions. No apparent ill effects were observed, which was superior to results obtainable for NS-100. Note that this represents a chlorine exposure of only 200 to 400 ppm-hr. A test duration of 20,000 to 30,000 ppm-hr would be necessary to meet today's definition of true chlorine *resistance*, as distinguished from some degree of chlorine *tolerance*.

The best salt rejections observed for the diallyl amine polymers were obtained not for the polyamide interfacial membranes, but rather for the corresponding polyureas. For example, poly(diallyl amine) homopolymer reacted interfacially with toluene diisocyanate yielded a membrane with 99.7% salt rejection at 20 gfd in a 600 psig test with 0.5% NaCl solution, whereas polyamide examples in the patent rarely exceeded 95% under comparable conditions. Unfortunately, the urea linkage would not be expected to withstand exposure to chlorine. In a study using model compounds, urea compounds rapidly degraded in chlorine exposure



Scheme 4.



Scheme 5.

tests, compared to slow degradation rates for amide compounds [68].

Kawaguchi and co-workers patented the use of several other types of polymeric polyamines as building blocks for interfacial composite membranes. These included amine-terminated low molecular weight polymers made by reaction of monomeric amines with monomeric polyepoxides [69], linear soluble polymers having pendant amine groups attached via carboxamide and sulfonamide side-groups [70], and aminated polymers formed from amine adducts with poly(2-chloroethyl vinyl ether) and with other halogen-containing polymers [71]. Also described in a patent was the use of additives in the polymeric amine solution that react to cause further crosslinking of the polymeric amine during a heat-cure [72]. Additives included esters, chlorohydrins, imidazoamides, and carbamates. To date, no composite reverse osmosis membranes are known to have been commercialized by Teijin corresponding to any of the above patents.

Hurndall, Jacobs and Sanderson [73] prepared composite membranes by reaction of polyvinylimidazoline with crosslinking agents on a porous polysulfone support. The polyvinylimidazoline was prepared by reaction of polyacrylonitrile with 1,2-ethanediamine, and the resulting polymer contained N-amino-ethylamide groups as well due to partial hydrolysis. The resulting copolymer has the structure shown in Scheme 5.

Crosslinking agents were isophthaloyl chloride, 3-chlorosulfonyl-benzoyl chloride and 3,5-bis-(chlorosulfonyl)benzoyl chloride. Reverse osmosis performance of up to 98.2% NaCl rejection at 23 l/m^2-hr was achieved, tested on 0.2% aqueous NaCl solution at 2 MPa and 20°C.

Interfacial polymerization with aliphatic monomeric amines: the NS-300 membrane

In the discovery by Cadotte of the NS-100 membrane, several monomeric amines had been tried as well as polyethylenimine. As shown in Table 2, taken from the first project report on NS-100 [29], these amines included both aliphatic and aromatic diamines, none of which provided attractive salt rejections when inter-

TABLE 2

Reverse osmosis performance of exploratory interfacial terephthalamide membranes

Amine reactant	Reverse osmosis data[a]	
	Water flux (gfd)	Salt rejection (%)
1,6-Hexanediamine	104	8.2
1,3-Propanediamine	233	30.6
1,2-Ethanediamine	too brittle to test	-
Hydrazine	too brittle to test	-
1,4-Benzenediamine	53	38
1,3-Benzenediamine	26.9	12
Piperazine	59.8	74
Polyethylenimine	29.3	96.3

[a]Test conditions: 3.5% synthetic seawater, 1500 psig, 25°C.

facially reacted with terephthaloyl chloride. These data appeared to confirm the comment in Morgan's book that such films would be porous to low molecular solutes. It was assumed for several years that polymeric polyamines were the only feasible route to high rejection composite membranes using interfacial polymerization, and the patent activity described above followed this line of reasoning. But, because of reports by Parrini and co-workers [74,75] of chlorine-resistant asymmetric membrane compositions based on piperazine-containing polyamides, Cadotte revisited the case of piperazine in interfacial composite membranes. He found that, through optimization of formation conditions, high rejection composite membranes could be made by interfacial reaction of piperazine with isophthaloyl chloride [33]. Salt rejections of as high as 98% were achieved in tests on synthetic seawater at 1500 psig [76].

Conditions necessary for obtaining good composite membranesof poly(piperazine-amides) included concentrations of 1 to 2% piperazine, use of an acid acceptor, and use of a surfactant in the amine recipe. A microporous polysulfone was soaked with the aqueous amine formulation, then well-drained or rolled on its surface with a soft rubber roller to remove excess reagent. This was followed by immersion in a hexane solution containing about 1% w/v isophthaloyl chloride. Isophthaloyl chloride was found to give better results than terephthaloyl chloride in this membrane preparation. Rigidity of the piperazine terephthalamide polymer may have been a factor. The best poly(piperazineamide) result in the 1500 psig synthetic seawater test was achieved with an amine formulation containing 1% piperazine, 1% sodium hydroxide and 0.5% sodium dodecyl sulfate, interfacially reacted with 1.0% isophthaloyl chloride. This membrane gave 26 gfd at 98% salt rejection. Unfortunately, seawater salt rejections of such membranes were more typically 96% or less, and reproducibility was a problem. Brackish water fluxes of these membranes were too low to elicit interest in their brackish water salt rejections. SEM micrographs of the surface of such membranes showed a very grainy structure, wherein the porosity between grains was likely to be filled only by making the interfacial membrane layer thick.

For best results in making poly (piperazineamide) composite membranes, the presence of an acid acceptor was necessary, whereas this was not a requirement in the case of the polyethylenimine and polyepiamine reactants. The formation rate of poly (piperazineamide) barrier layer was slow, needing higher concentrations of the acyl halide along with the acid acceptor to promote polyamide formation. This was so despite the relatively strong basicity of this secondary amine. One may speculate that piperazine ineffectively partitions into the organic phase, then tends to be tied up as the hydrochloride salt, forestalling progress of the polyamide-forming reaction, and this is ameliorated by the use of the acid acceptor. In the case of polyethylenimine, the high proportion of tertiary amine content acts as a built-in acid acceptor.

The surfactant in the aqueous piperazine solution can be replaced in some cases by water-soluble polymers, with good results. One such polymer is poly(vinyl alcohol) [77]. Cationic polymeric wetting agents, such as polymeric methacrylates containing pendant labile sulfonium salts, can also be used with good effects [78].

Replacement of a portion of the isophthaloyl chloride with a triacyl halide – 1,3,5-benzenetricarbonyl chloride (commonly referred to as trimesoyl chloride) – was tried by Cadotte as possible way to modify the membrane's flux or salt rejection [76,79]. Dramatic and unexpected changes in flux and salt rejection resulted. The results are illustrated in Table 3. When the ratio of diacyl to triacyl chloride was

TABLE 3

Reverse osmosis test data on a series of poly(piperazineamide) membranes

Acyl halide			Seawater test[a]		$MgSO_4$ test[b]	
IPC	TMC	Acid acceptor	Flux (gfd)	Salt rej. (%)	Flux (gfd)	Salt rej. (%)
1.0	0.0	1.0% NaOH	26	98	4	99.2
0.9	0.1	0.9% Na_3PO_4	33	96	18	99.0
0.8	0.2	0.9% Na_3PO_4	73	78	58	99.9
0.67	0.33	0.9% Na_3PO_4	94	65	77	99.6
0.5	1.5	0.9% Na_3PO_4	96	64	31	99.9
0.0	1.0	1.0% Me_2Pip	80	68	26	99.3

Key: IPC and TMC = isophthaloyl and trimesoyl chloride; NaOH = sodium hydroxide; Na_3PO_4 = sodium phosphate; and Me2Pip = N,N'-dimethylpiperazine.

[a]Seawater test conditions: 3.5% synthetic seawater, 1500 psig, 25°C.

[b]Brackish water test conditions: 0.5% MgSO4, 200 psig, 25°C.

varied from 100:0 to 0:100, seawater rejections fell but magnesium sulfate ($MgSO_4$) rejections held steady at 99% and higher. Water flux went through a maximum at roughly 50:50 w/w diacyl:triacyl chloride content. The data in Table 3 did involve some changes in the acid acceptor for best flux and $MgSO_4$ rejection at each condition. The shape of the flux curve could vary with changes in acid acceptors in the piperazine solution formulations.

The combination of high flux and high $MgSO_4$ rejection was of sufficient practical interest to assign the name NS-300 to the piperazine–trimesoyl chloride membrane. The NS-300 membrane exhibited anion-selective salt rejection characteristics. This is illustrated by the data in Table 4. In a sequential series of reverse osmosis tests on the same single specimen of membrane, low rejections were seen for salts with monovalent anions (chloride), but high rejections for salts with divalent anions (sulfate). No significant selectivity was noted between monovalent (sodium) and divalent (magnesium) cations. The results strongly suggested an anionically charged poly (piperazineamide) barrier layer. That could come about through partial hydrolysis of the acyl halide groups, i.e. the NS-300 membrane most certainly contained carboxylic acid groups. A resulting Donnan ion repulsion effect accounted at least in part for the consistently high sulfate rejections. It also accounted for the lower rejection of chloride ion at higher salinity levels (0.5% vs. 0.1% NaCl), where increased shielding of the Donnan ion repulsion force occurs. Assuming hydrolysis as a side reaction, the chemistry of the membrane would be as shown in Scheme 6.

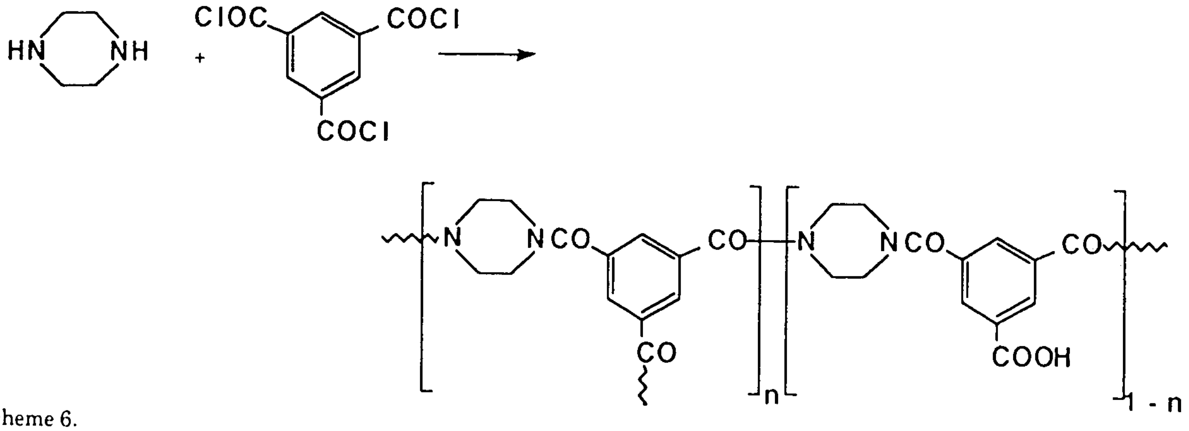
TABLE 4

Effect of cation/anion charge on the rejection of various salts by the piperazine trimesamide interfacial membrane

	Reverse osmosis test data[a]	
Salt solution	Salt rejection (%)	Flux (gfd)
0.1% $MgSO_4$	98.0	35
0.1% NaCl	70	31
0.5% NaCl	50	42
0.5% Na_2SO_4	97.8	41
0.5% $MgCl_2$	46	32
0.5% $MgSO_4$	97.8	32

[a]Test conditions: 200 psig, 25°C.

A study of acid acceptors showed that the



Scheme 6.

TABLE 5

Seawater reverse osmosis performance of poly(piperazineamide) membranes made from piperazine-terminated oligomers

Reactant used to prepare oligomer	Acid acceptor	Reverse osmosis test data[a]	
		Flux (gfd)	Salt rej. (%)
Trimesoyl chloride	NaOH	13	99.0
Trimesoyl chloride	Et_3N	58	93.8
Cyanuric chloride	NaOH	14	99.2
Cyanuric chloride	Et_3N	24	98.0
Phosphorous oxychloride	N,N′-dimethylpipreazine	45	93.9
1:1 Trimesoyl: isophthaloyl Cl	Et_3N	34	92.4

[a] Seawater test conditions: 3.5% synthetic seawater, 1500 psig, 25°C.

base strength of the acid acceptor affected the degree of concurrent hydrolysis [80]. Sodium hydroxide produced NS-300 membranes with the lowest overall salt rejections. Weak bases such as N,N′-dimethylpiperazine and sodium dihydrogen phosphate gave the highest salt rejections. SEM studies showed that the surface morphology of the poly(piperazineamide) membranes of Table 3 changed as a function of triacyl content [27]. Structures varied from a grainy surface for the isophthalamide to a swollen-like, crenelated structure for the trimesamide.

Poly(piperazineamide) composite membranes made from a blend of isophthaloyl and trimesoyl chlorides were tested on a brackish feedwater in a long term government-supervised test at Roswell, NM [81]. The membranes were exposed to an average of 0.75 ppm active chlorine in a 3600 ppm chloride-sulfate brackish water at pH 5.5 for about 2,500 hr. TDS rejections were in the range of 55–65% for the first 2,400 hr, but fell off rapidly thereafter, along with increasing flux. The results indicated that this poly(piperazineamide) membrane was not fully chlorine-resistant. It should be noted, however, that the system was found to be heavily contaminated with iron deposits, which may have promoted chlorine attack on the poly(piperazineamide) membrane.

An alternative way of making interfacial membranes of piperazine was to prepare prepolymers or oligomers of piperazine that were amine-terminated. For example, trimesoyl chloride could be reacted with an excess of piperazine, and the resulting piperazine-terminated oligomer then interfacially reacted with isophthaloyl chloride to form the composite membrane. Several oligomeric compositions were made by reacting piperazine with one or more acyl halides in 1,2-dichloroethane [76,79,80]. The oligomers precipitated from this solvent, the precipitation acting as a way of molecular weight control. The oligomers were taken up in water, filtered to remove gels and insoluble fractions, then interfacially polymerized with isophthaloyl chloride *in situ* on the surface of polysulfone supports. Results of synthetic seawater tests on these various membranes are shown in Table 5. The best result was 99.2% synthetic seawater rejection, but at a relatively low flux of 14 gfd, considering the 1500 psig test pressure.

The NF-40, NTR-7250, UTC-20/50/60 and ATF-50 poly(piperazineamide) membranes

Several commercial membranes have appeared which utilize the basic chemistry of the NS-300 membrane approach. Chief examples are the NF-40 membrane made by FilmTec Corporation, the NTR-7250 membrane made by the Nitto Denko Company (Nitto Electric Industrial Co.), and the UTC-20 and UTC-60 membranes made by Toray Industries. All are thin film composite membranes made by interfacial polymerization on a polysulfone base.

The barrier layer in the FilmTec® NF-40 membrane is known to be essentially the interfacial reaction product of piperazine with trimesoyl chloride, and to be an anionically charged membrane. It is designated by FilmTec as a *nanofiltration* membrane, the term nanofiltration drawn from the observation that size selectivity of the membrane towards non-charged solutes approximates 10 Å, i.e. a one nanometer cutoff. Figure 7, adopted from Egli et al. [82], illustrates the performance range of nanofiltration membranes, which stand at the interface between reverse osmosis and ultrafiltration membrane processes. The NF-40 membrane showed a pure water flux of about 25 gfd at 225 psig, temperature operating capability from 0 to 45°C, and pH resistance from 2 to 11. Rejection data for the NF-40 membrane toward a series of corn syrup sugars were: glucose, 90%; maltose, 98%; and maltotriose, 99+%. The technique of using corn syrups for determination of molecular weight cutoffs of reverse osmosis and nanofiltration membranes is described in a publication by Cadotte et al. [83] (wherein a tight "NF-40LF" membrane was characterized, as well as other competitive membranes).

Water and salt transport properties of the NF-40 membrane were studied by Eriksson [84]. The impact of the contribution of Donnan ion repulsion effects as a function of chloride and sulfate salt concentrations is illustrated in Fig. 8. This type of behavior has led to applications of this membrane in salt whey treatment (concentration of sugars and proteins with simultaneous reduction of NaCl by membrane passage), sulfate removal from seawater, recycle of waste dye streams, and recycle

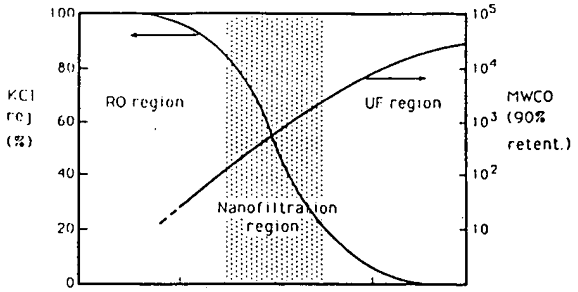


Fig. 7. Diagram of the region of nanofiltration membrane performance relative to reverse osmosis and ultrafiltration membranes [82].

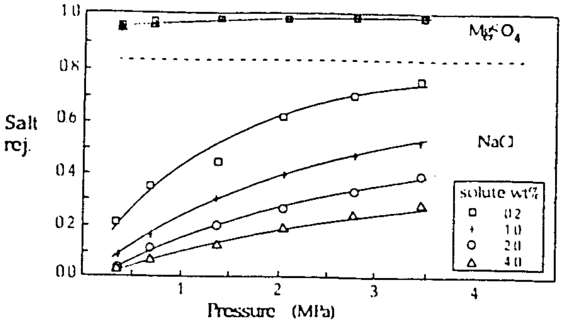


Fig. 8. NF-40 membrane salt rejection performance toward $MgSO_4$ and NaCl at different ionic strengths as a function of operating pressure (and hence, flux) [84].

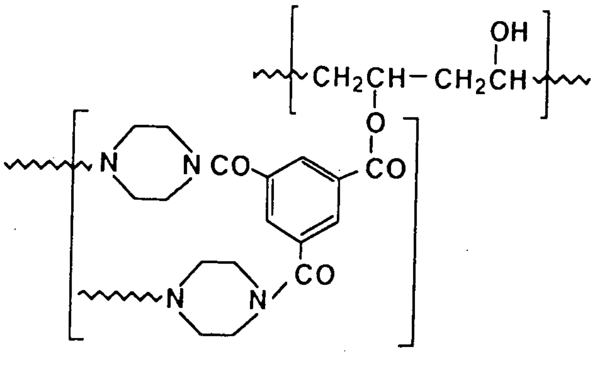
of melamine-based anionic electrophoretic paints for aluminum surface finishing [85,86]. This membrane has also been examined for its utility in color removal from bleach effluents in the wood pulping process where it performed well [87], and in sodium ion separation from hardness ions in a textile mill scour effluent [88]. The barrier layer composition in the NF-40 membrane has been approved for repeated food contact by FDA [89].

A high flux, low pressure version of this membrane, designated as NF-40HF, was commercially available for a short time [90], but proved to be marginally resistant to pH extremes. A new version, designated as XP-45, is under development by FilmTec, and matches the NF-40HF in terms of flux versus pressure, while exhibiting improved pH resistance and better solute rejection control than both NF-40 and NF-40HF [91].

The Nitto Denko membrane designated as NTR-7250 was commercially introduced contemporaneously with FilmTec's NF-40 membrane [59]. The initial market thrust of this membrane was for final filtration of ultrapure water in semiconductor chip manufacturing, where the claimed chlorine resistance of this membrane was seen as an advantage for system disinfection and sterilization. NTR-7250 membrane exhibits flux and rejection data essentially on a par with the NF-40HF membrane [59,92], but has an upper pH limit of 9. Composition of the membrane barrier layer is believed to involve a combination of poly(vinyl alcohol) and piperazine trimesamide.

A corresponding Nitto Denko patent [93] describes a membrane made by the interfacial reaction of trimesoyl chloride with an aqueous solution containing 0.25% piperazine, 0.25% poly(vinyl alcohol), and 0.5% sodium hydroxide, and having a 110°C heat-curing step for insolubilization of the poly(vinyl alcohol) layer. The resulting membrane exhibits about 99% $MgSO_4$ rejection and 30 gfd, tested at 200 psig on a 500 ppm feedwater. The patent claims a discrete layer of insolubilized poly(vinyl alcohol) resting upon a microporous support, and a poly(piperazineamide) barrier layer resting upon the poly(vinyl alcohol) layer. The method of making the membrane allows concurrent esterification of poly(vinyl alcohol) by trimesoyl chloride during amide formation, which correlates with the an alkaline pH limit of 9 stated for NTR-7250. Ohya [94] provided a formula for the NTR-7250 membrane that indicated the following barrier layer composition (Scheme 7).

Another membrane made by Nitto Denko appears to be closely related to NTR-7250, i.e. the NTR-729HF membrane. The NTR-729HF membrane is covered in a later section of this review under the subject of poly(vinyl alcohol)-based composite membranes.



Scheme 7.

The UTC-20, UTC-50 and UTC-60 *u*ltra*t*hin *c*omposite membranes, which correspond to the Toray SU-200, SU-500 and SU-600 series of spiral element products, contain poly- (piperazine-amide)-based barrier layers, and are listed as such in Table 1 of a recent publication by Kurihara and Himeshima [95]. Beyond this listing, the specific composition of these membranes is not revealed. However, Kurihara and co-workers [96] have described the performance characteristics of two UTC-20 versions, along with two UTC-40 membrane versions (composition unstated). A UTC-20HR version exhibited 2.4 m^3/m^2-day (60 gfd) flux and 70% NaCl rejection, tested at 15 kg/cm^2 on 1500 ppm aqueous NaCl solution. A high flux version, UTC-20HF, exhibited 3.5 m^3/m^2-day flux and 50% NaCl rejection under the same conditions. NaCl rejections were higher at higher dilutions, and lower as concentrations exceeded 1500 ppm, as was typical for poly(piperazineamides). Chlorine resistance was noted to be similar to findings with the NS-300 membrane, and being not quite as high as for cellulose acetate. The UTC-20 membranes appeared to have been initially aimed at competing with the NTR-7250 membrane in the ultrapure water filtration market.

The ATF-50 membrane is a commercial poly(piperazineamide) composite membrane recently introduced by Advanced Membrane Technology, Inc., and has performance characteristics similar to the NF-40 and NTR-7250 membranes. Product literature on ATF-50 listed average flux of 60 gfd (225 psig, 25°C) and solute rejections of 69% for NaCl and 99% for lactose, tested on 2000 ppm feed concentrations. A higher flux version, ATF-30, is under development, that would exhibit about 35% NaCl rejection and 98% lactose rejection.

Patterson Candy International (PCI) has apparently prepared poly(piperazineamide) membranes in tubular form for use in its tubular reverse osmosis systems. A poly (piperazineamide) composite membrane has apparently also been prepared in commercial form in Russia, presumably by Vladimir NPO Polymersintez.

In view of all these commercial membrane offerings utilizing composite poly(piperazineamide) technology, one can anticipate that further examples of composite poly- (piperazineamides) will appear in the commercial marketplace in time.

Interfacially formed membranes from aliphatic amines other than piperazine

With regard to other aliphatic amines in composite membranes, data were published by Petersen and co-workers [97] comparing 1,2-ethanediamine, 1,4-cyclohexanediamine and 1,3-bis(aminomethyl)cyclohexane with piperazine when converted into trimesamides. These data are shown in Table 6. The three amine trimesamides all showed higher sodium chloride rejection than the poly(piperazineamide), and were generally much lower in their water permeability. The presence of amidic hydrogen in the polyamide linkage was speculated to provide strong interchain bonding forces. This counteracted the hydrophilic swelling forces caused by the presence of any carboxylate groups. The lowest fluxes were associated with 1,2-ethanediamine, wherein the highest population of amidic hydrogen would be present, even though the resulting trimesamide would have an amide:methylene group ratio equivalent to the piperazine trimesamide.

McCray [98] has interfacially reacted *p*-xylylenediamine (bis-1,4-aminomethylbenzene) with blends of isophthaloyl and trimesoyl chloride to form composite reverse osmosis membranes, in which the amide linkage involves the aliphatic $-CH_2NH_2$ moiety. A combination of high flux, high salt rejection, and good chlorine resistance was claimed. The interest focused on this membrane arose from a study of the chlorine susceptibility of model compounds at Bend Research [68]. In that study, monomeric polyamines were concluded to be capable of forming chlorine-stable polyamide membranes if the amide nitrogen atoms were not directly bound to aromatic rings. McCray [99] also prepared a composite membrane by interfacial reaction of isophthaloyl chloride with a tetra-imino compound, $C(CH_2NHMe)_4$, obtaining a performance of 64% NaCl rejection and 111 gfd at 800 psig on 0.5% NaCl solution.

The BR-101, TTM-20, TTM-60 and TTM-99 membranes

The interfacial composite membranes developed by McCray and others at Bend Research Institute are currently undergoing commercial development at AquaAir Environmental, Inc [100]. These membranes are in the form of hollow fiber composites in which the ultrathin barrier layer is formed on the lumen wall of a high burst strength, microporous polysulfone hollow fiber. Improved resistance to fouling is seen for this type of reverse osmosis membrane configuration. The BR-101 membrane consists of the interfacial reaction product of *p*-phenylenediamine with trimesoyl chloride. The

TABLE 6

Reverse osmosis performance of interfacial trimesamide membranes formed from various aliphatic diamines

Amine reactant	Reverse osmosis test data[a]			
	0.2% $MgSO_4$		0.2% NaCl	
	Flux (gfd)	Salt rej. (%)	Flux (gfd)	Salt rej. (%)
1,2-Ethanediamine	1-6	99	1-6	95-97
1,4-Cyclohexanediamine	13-23	98-99	15-36	71-81
1,3-Cyclohexane-bismethylamine	15-18	96	11-14	85-94
Piperazine (control)	28	97	37	53

[a]Test conditions: 200 psig, 25°C.

TABLE 7

Reverse osmosis performance of AquaAir environmental interfacial polyamide membranes

Solute	Reverse osmosis test data[a]							
	BR-101		TTM-99		TTM-60		TTM-20	
	Gfd	Rej%	Gfd	Rej%	Gfd	Rej%	Gfd	Rej%
0.5% $MgSO_4$	12	99.5	70	99.5	120	95	120	70
0.5% NaCl	12	99.5	60	98.5	120	60	120	20
3.5% seawater	7	99	30	98.5	-	-	-	-

[a]Test conditions: BR-101, TTM-60 and TTM-20 at 400 psig on $MgSO_4$ and NaCl; BR-101 at 600 psig on seawater; TTM-99 at 800 psig on all three solutes; 25°C and pH 6.

TTM-20 and TTM-60 membranes are nanofiltration-type composites wherein the barrier layers consist of tetrakis-(N-methyl-aminomethyl)methane reacted with isophthaloyl and with trimesoyl chloride, respectively. The NaCl rejection of these two TTM membranes corresponds to their numbering. The TTM-99 membrane is a high rejection membrane with an as yet proprietary composition. Table 7 provides flux and salt rejection data for these membranes towards different salt solutions [100]. In addition to the usual applications of thin film composite reverse osmosis membranes, the TTM-20 and TTM-60 membranes are capable of treating oil-containing aqueous feedstreams, since the lumen flow geometry greatly mitigates oil fouling tendencies.

Interfacial polymerization with aromatic monomeric amines: the FT-30 membrane

In 1978 during efforts to improve the performance of poly(piperazineamide) membranes, Cadotte [101] discovered that composite membranes having an excellent combination of high rejection and high flux under seawater test conditions could be made by interfacial polymerizations of monomeric aromatic amines with *aromatic* acyl halides. A key factor was the use of an acyl halide or mixture of acyl halides having a functionality greater than 2.0, i.e. at least one of the acyl halides had to have three or more carbonyl halide groups. Best results were obtained using trimesoyl chloride alone as the acyl halide. 1,3-Benzenediamine (*m*-phenylene-diamine) gave the best results insofar as the aromatic amine. Another key factor was the avoidance of a heat-cure. Residual unreacted aromatic amine tended to seal off the surface of the underlying polysulfone support during heating, causing low flux.

A typical recipe for this fully aromatic polyamide membrane consisted of a 2.0% 1,3-benzenediamine solution in water coated onto polysulfone, then interfacially contacted with a 0.1% w/v solution of trimesoyl chloride in 1,1,2-trichlorotrifluoroethane or in hexane. Fabrication conditions differed from the NS-300 membrane case in several respects. Addition of acid acceptors was not required; in fact, acid acceptors tended to give membranes with poorer salt rejection. No surfactant was required either; surfactants tended to harm the properties of the membrane. Acyl halide concentrations were only 1/3rd to 1/10th the concentrations needed in the case of NS-300. Despite these differences, interfacial formation of the crosslinked aromatic polyamide barrier layer appeared to proceed at a significantly faster pace than for piperazine.

When an amine recipe containing equal parts of piperazine and 1,3-benzenediamine was utilized, the aromatic amine monomer was the dominant reactant as evidenced by the properties of the resulting membrane. A combination of partition coefficients and reaction rates appeared to favor aromatic polyamide formation, with piperazine possibly also being diverted into the role of acid acceptor.

In the case of poly(piperazineamide) membranes, water-soluble oligomers could be prepared and used in subsequent interfacial polymerizations to generate examples with good salt rejections. However, in the case of the aromatic amines, this approach was not useful. The corresponding aromatic amide oligomers showed extremely poor solubility in water. Rak and Ward [102] patented a route past this obstacle, wherein they reacted 1,3-benzenediamine with trimellitic anhydride acid chloride as a first step. The oligomeric product contained both amino groups and carboxylate groups, the latter generated by opening up of the anhydride group. This oligomeric product was solubilized by means of the alkali salt of the carboxylate function. Some carryover of monomeric aromatic amine, present in the initially formed oligomer as the amine carboxylate salt, was possible in this preparative route.

SEM photomicrographs of the surface of interfacial membranes of monomeric aromatic amines reacted with trimesoyl chloride showed a unique and characteristic ridge-and-valley structure [1], shown in Fig. 9. When aliphatic amines were used, surfaces were either smooth or grainy. Even in the case of 1,3-xylylenediamine (1,3-bis-aminomethylbenzene), which is an aromatic-ring-substituted *aliphatic* amine, a grainy surface was observed rather than the ridge-and-valley structure. On the other hand, the ridge-and-valley structure was observed even when the acyl halide had been changed to a cycloaliphatic compound (1,3,5-cyclohexane-tricarbonyl chloride), and thus seems to be associated specifically with the monomeric aromatic amine.

The average thickness of the barrier layer in the metaphenylene trimesamide product has been estimated to be 2000 Å. In an electron microscopy study of membranes by Uemura and Inoue [103], the barrier layer thickness of a phenylenediamine trimesamide membrane (FilmTec® FT-30 membrane) was reported to vary from 400 Å (valley) to 2600 Å (ridge top).

The interfacially synthesized aromatic polyamide membrane is mildly anionic in charge, indicating some hydrolysis of acyl halide groups to carboxylic acid groups. It is susceptible to binding and fouling by cationic surfactants. For instance, exposure to a quaternary germicide such as benzalkonium chloride (a mixture of alkyl dimethyl benzylammonium chlorides) causes up to a 50% flux loss due to absorption of this cationic surfactant. Anionic surfactants show comparatively minor absorption effects. This behavior is in contrast to the case of polyethylenimine-based membranes which exhibit a weak cationic charge and are poisoned by anionic surfactants. The absorption of sur-

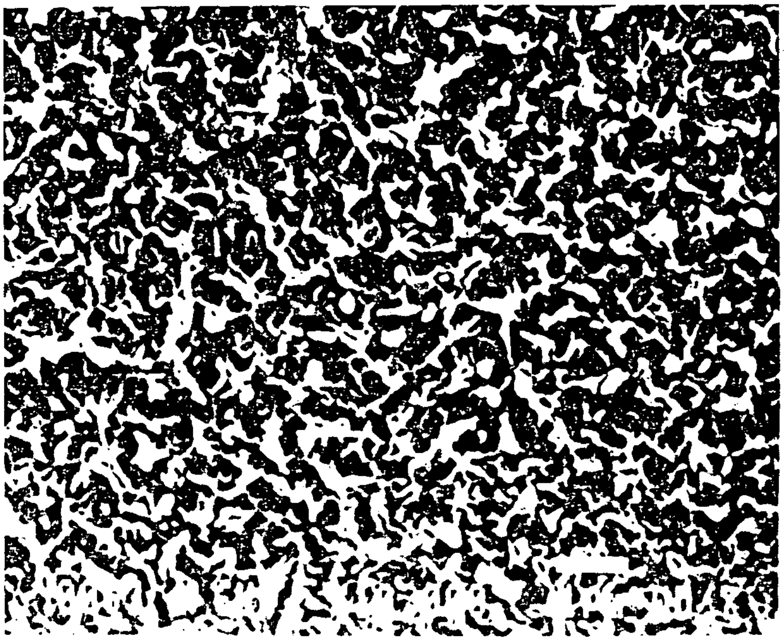


Fig. 9. SEM photomicrograph of the surface of the barrier layer formed from interfacial reaction of 1,3-benzenediamine with trimesoyl chloride, showing a ridge-and-valley structure [1].

factants, with attendant flux loss, is at least partially reversible, but rinse-out can be a very lengthy process.

Salt rejection as a function of pH was found to reach a maximum at pH 8 to 9 for this membrane composition, in contrast to the pH 5.5 maximum of the polyepiamine-based composite membrane. Figure 10 illustrates the seawater rejection dependence of a metaphenylene trimesamide membrane on pH [104], showing its general applicability through the pH range of 5 to 11. Below pH 5, acid transport through the membrane accounted for the fall-off in salt rejection, which was measured by conductivity of the permeate.

Cadotte's discovery was developed at FilmTec Corporation into a new reverse osmosis membrane product designated FT-30. The chemistry of FilmTec® FT-30 membrane may be described as shown in Scheme 8.

The composition of the barrier layer in terms of the carboxylate-bearing amide moiety in the idealized formula below has been estimated from ESCA studies [105] to be approximately $n=0.72$. This reflected carboxylic acid content on the membrane surface, but may not have necessarily been representative of carboxylate content in the bulk of the barrier layer. Carboxylate content could vary from membrane sample to sample, depending on the purity of the acyl halide reactant, any pre-hydrolysis of acyl halide by moisture contained in the organic solvent, presence of certain contaminants in the amine solution (particularly N,N-dimethylformamide), and processing conditions. The sensitivity to cationic surfactants was universal for all such samples, however.

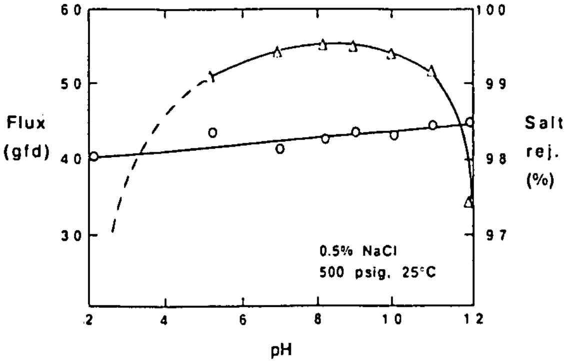
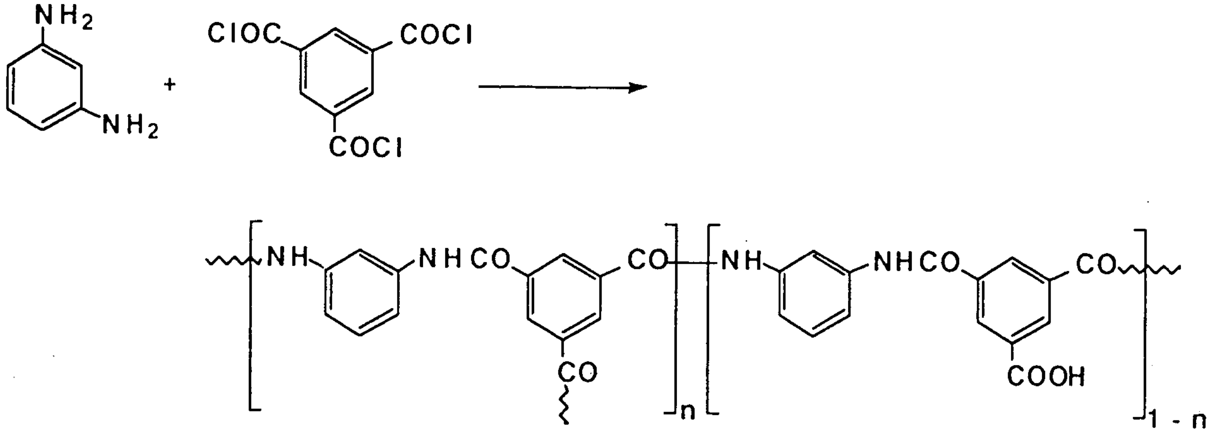


Fig. 10. Salt rejection and flux as a function of pH for a metaphenylene trimesamide (FilmTec FT-30) composite membrane [104].

Carboxylate generation by interaction of acyl halides (such as trimesoyl chloride) with N,N-dimethylformamide is especially noteworthy. N,N-Dimethylformamide is commonly used in the casting of polysulfone supports, and some carry-forward into the aqueous amine solution can be anticipated. This compound is known to react with an acyl chloride to produce an amidinium chloride. The amidinium chloride is relatively unreactive toward an aqueous aromatic amine, and would be eventually hydrolyzed to a carboxylate group. Higher residues of carboxylate content would be expected to generate higher water fluxes in these membranes. This expectation is borne out by results in a patent issued to Chau [106], wherein aprotic solvents (especially N,N-dimethylformamide) are added to the aqueous aromatic amine solution. Such behavior by N,N-dimethylformamide can also be inferred from experimental data in an earlier patent issued to Sundet [107]. Specific addition of N,N-dimethylformamide to the acyl halide solution has also been used by Toray Industries [108,109], presumably in part for the same purpose. For example, one recipe called for addition of 225 ppm of N,N-dimethylformamide to a 0.1% solution of 1:1 trimesoyl chloride:terephthaloyl chloride [109].

Water and salt transport properties of the FT-30 membrane were studied by Eriksson [84] and compared with the NF-40 poly(piperazineamide) membrane. Forgach et al. [110] also studied the transport characteristics of sheet and composite hollow fiber metaphenylene trimesamide membranes and measured the reflection coefficients, salt



Scheme 8.

permeances and hydraulic permeances of the membranes. Mehdizadeh and Dickson [111] have applied a modified surface force-pore flow transport model to the FT-30 membrane with satisfactory prediction of water/NaCl permeation behavior. The effects of temperature on flux and solute rejection of the FT-30 membrane over the temperature range of 5 to 60°C at 350 to 7000 kPa have been modeled by Mehdizadeh et al. [112].

Commercial variations of this membrane have been developed for municipal tapwater purification (TW-30 series), brackish water conversion (BW-30 series) and seawater conversion to potable water (SW-30 and SW-30HR series). Versions of the membrane in sheet form have been manufactured under license as HR-95 and HR-99 by De Danske Sukkerfabrikker Filtration Products (recently became Dow Danmark Separations Systems) for applications in plate-and-frame modules. A tubular version of the FT-30 membrane is also being manufactured under license by Patterson Candy International (now part of the Thames Water Authority) for applications in the food industry such as concentration of apple, orange and tomato juices [113]. The membrane has been designated ZF99, and tubular modules of the membrane as AFC99. The interfacial polyamide of the FT-30 membrane has been approved by FDA for food contact use [114].

The performance properties of the FT-30 membrane have been summarized in several publications by FilmTec [104,115–117]. The TW and BW products are capable of about 25 gfd flux under test conditions of 0.2% NaCl feedwater and 225 psig pressure. This represented about a 40 to 50% reduction in the operating pressure required in municipal water treatment installations vis-à-vis commercial cellulose acetate and noncellulosic membranes in use at the time these FT-30 products were introduced in the early 1980s. Crowdus [118] has pointed out the impact this made on design and costs of reverse osmosis installations. Other publications on purified water preparation using BW-30 membranes have appeared as well [119,120].

The SW-30 membrane products can generate up to 25 gfd and 99.1% salt rejection, operating on standard seawater at 800 psig. The SW-30HR membrane products provide about 17 gfd at 99.3–99.5% salt rejection, operating on standard seawater at 800 psig. The latter membrane is increasingly used in seawater desalination plants requiring single-pass operation at recoveries of up to 45% recovery (i.e. potable water as a percentage of incoming feedwater)

[121]. In this respect, it is the first spiral-wound membrane product to compete broadly and effectively in seawater desalination with the DuPont Permasep® hollow fiber permeators since the latter's commercial introduction in 1972.

Bhattacharyya and co-workers have studied the use of FT-30 membrane products for treating various wastewaters [122–125]. Examples included coal-liquefaction wastewaters contaminated with phenolic compounds. Rejections of phenolic compounds were highest when they were converted to salt form with alkali. Some binding of phenols to the crosslinked aromatic polyamide barrier does occur at neutral pH, causing a decrease in water flux. Schutte and Belfort [126] measured the permeability of FT-30 membrane to a homologous series of phenols and a homologous series of alcohols. They successfully modeled the solute permeabilities of these two series, using a simplified version of a comprehensive theory of solute, solvent and membrane interactions.

Because of the presence of amidic hydrogen in the amide linkages of this membrane, no tolerance to chlorine might be expected. Yet, the membrane proved to have a surprisingly better chlorine tolerance than the polyethylenimine- and polyepiamine-based membrane types. The *m*-phenylene trimesamide composition showed roughly 1000 ppm-hr of chlorine tolerance, enough to withstand a short chlorine upset in an operating reverse osmosis installation. The rate of chlorine attack was examined as a function of pH [8]. Attack was fastest under alkaline conditions, i.e. pH 8 to 12, at which pH the active species is hypochlorite ion. At pH 5, the rate of chlorine attack was much slower, even though at this pH the active ingredient is the more potent form – hypochlorous acid. At pH 3, membrane failure occurred because of selective chlorination and embrittlement of the underlying polysulfone support.

Iron was shown to promote chlorine attack. FT-30 membranes impregnated with ferric ion by pretreatment with ferric chloride were rapidly degraded upon exposure to hypochlorite in contrast to untreated controls [1]. Other heavy metals may also act as catalysts for chlorine attack. A study by Murphy [127] on premature cellulose acetate membrane failure due to damage by chlorinated water pinpointed chromium and cobalt salts as catalysts of this damage. Peplow and Vernon [128] have detected deposits of iron, copper, zinc, chromium, lead and vanadium on the surfaces of seawater desalination membranes, the chromium arising from corrosion of stainless steel piping. Kurihara and Himeshima [95] have pointed out that manganese ion can be oxidized to permanganate ion by hypochlorite in the presence of copper ion as a catalyst, as found by Lister; [129] permanganate ion will also attack polyamide membranes.

Glater and co-workers [130,131] have studied the mechanism of attack of halogen disinfectants on aromatic polyamide membranes and found that halogenation of the amino-substituted aromatic ring occurred. Avlonitis et al. [132] also examined the effect of chlorine on asymmetric aromatic polyamide membranes, confirmed the presence of ring chlorination, and concluded that membrane properties deteriorated due to transformation of crystalline structures to amorphous structures in the polyamide during chlorination. Neither group appeared to attribute polymer chain scission as a contributing factor. Koo and co-workers [105,133] examined the mechanism of chlorine attack on FT-30 membrane, utilizing ESCA. Chlorination of the amine ring occurred, and the rise in overall content of permanently bound chlorine correlated with a loss of salt rejection and rise in water flux. (GC-MS analysis of hydrolysates of chlorine-exposed *m*-phenylene trimesamide barrier layers will show presence of monochloro and dichloro derivatives of 1,3-benzenediamine, and even a trichloro derivative in trace amounts.) ESCA spectra also showed a build-up of carbonyl groups, which indicated a concomitant oxidation of amine rings, possibly to quinoid-type moieties. This appeared to be in some way associated with cleavage of amide linkages. The pH dependence also implies a base-promoted chain cleavage step. The barrier layer becomes increasingly anionic in character with progression of chlorine attack, as was found in a long term exposure of the membrane to chlorinated municipal tapwater wherein Donnan ion repulsion effects became demonstrable [81]. The polyamide structure can completely disappear upon prolonged exposure to high chlorine levels.

A U.S. patent by Swedo and Zupancic [134] claims improved chlorine tolerance of interfacial aromatic polyamide membranes if the monomeric aromatic amine is 4-chloro or 5-chloro-1,3-diaminobenzene. However, presence of an electron-withdrawing group on the amine ring does not seem to be the answer to improved chlorine tolerance, in light of the above. In their results, the ring chloro group exhibited a sizable flux-reducing effect versus nonchlorinated aromatic diamines.

In seawater desalination installations utilizing FilmTec SW30HR membrane modules, the most stable performance was obtained when the incoming seawater was disinfected with chlorine, then treated with enough bisulfite ion to remove both residual chlorine and all dissolved oxygen. This result raised the question of long term stability of this interfacial membrane to dissolved oxygen. A study by Eriksson [135] showed that FilmTec® SW-30 membrane was stable to long term (one year) exposure to dissolved oxygen at levels of 27 mg/l. Based on this and other operational data, it was concluded that operation of a seawater desalination plant under anaerobic conditions was preferred because of promotion of biofouling by oxygenated feedwater, but not because of any oxygen sensitivity of the membrane composition. For surface sources or polluted well sources of seawater, biogrowth was far less of a problem under anaerobic conditions.

Constantini and co-workers [136] examined the suitability of a peracetic acid preparation as a sterilizing agent for FT-30 spiral-wound membrane elements. They found it to be effective for repeated sterilizations of FT-30 elements used for production of dialysate water in a hemodialysis clinic. Product literature for the FT-30 membrane indicated that hydrogen peroxide resistance of the membrane was limited to low concentrations (25 ppm) at 25°C, at apparently neutral pH. It may be that membrane stability to hydrogen peroxide is greatly increased at acidic pHs (e.g. pH 3), such as is found in peracetic preparations, since such preparations are high in hydrogen peroxide content. Formaldehyde can also be used for sterilization of FT-30 membrane elements, but is objectionable because of concerns about its potential carcinogenicity. Adams [137] examined the compatibility of chlorine dioxide with several reverse osmosis membranes, including the FT-30 membrane. At a dosage level of 1 ppm, only very small performance declines were seen through six months of testing. A portion of the chlorine dioxide passed through the membrane providing a residual in the permeate.

As noted earlier, the interfacial reaction of 1,3-benzene-diamine with trimesoyl chloride generates some carboxylate groups by a concomitant hydrolysis reaction. The crosslinked aromatic polyamide barrier layer also contains a significant residue of terminal unreacted amine groups. Acid transport through FT-30 membranes is probably promoted by the pendant amino groups. These can be derivatized with amine-reactive compounds such as propanesultone or active vinyl compounds [138]. The derivatized compositions typically show higher rejections of mineral acids and small organic solutes (e.g. isopropanol) than the nonderivatized analogs. Oxidation of the residual amine groups by means of peracetic acid or other selected oxidants also improves mineral acid rejections [139]. Derivatization with aromatic diazonium salts is also possible, presumably by coupling to the aromatic amine residues in the membrane [140].

The TFCL, CPA2/NTR-759 and Membrafil polyamide membranes

In 1987, UOP Fluid Systems introduced a new commercial membrane designated as TFCL®. A high pressure version suitable for seawater desalination and a low pressure version suitable for brackish water treatment were developed [141]. It was initially described as a newly introduced chlorine tolerant TFC membrane, having generally at least 1000 ppm-hr of tolerance to incompletely dechlorinated feedwater. This membrane consists essentially of the reaction product of 1,3-benzenediamine with trimesoyl chloride, rather than a version of the polyepiamine-based TFC® membranes. (For sake of reference, an analytical method for determining the chemical composition of an interfacially formed aromatic polyamide barrier layer is given in Example 27 of U.S. patent 4,761,234 [142].)

Operating properties of the TFCL membrane were described in publications by Light and co-workers [143–145]. Data were consistent with a membrane consisting of essentially the same chemistry as the FilmTec FT-30, including matching curves for chlorine resistance and for pH effect on maximum salt rejection, and sensitivity to quaternary surfactants. The TFCL membrane has since become the subject of an ongoing patent infringement suit instituted by FilmTec Corporation against Allied-Signal, Inc. (the parent firm of UOP Fluid Systems). For most of 1990 and 1991, the TFCL membrane was unavailable in the U.S. because of a court-imposed preliminary injunction against its manufacturer.

The CPA2 reverse osmosis membrane is a composite polyamide membrane first introduced as a commercial product in the U.S. on or about the beginning of 1990 by Hydranautics, Inc. An equivalent reverse osmosis membrane designated NTR-759 is available in Japan from Nitto Denko, the parent company of Hydranautics. The barrier layer of the CPA2 membrane is essentially a copolyamide derived from the reaction of 1,3-benzenediamine with a blend of isophthaloyl and trimesoyl chlorides. For much of 1991 and 1992, it was unavailable commercially in the U.S. as a result of a court judgement that the CPA2 membrane infringed the FilmTec basic patent on interfacial aromatic polyamide composite membranes. A new membrane designated NCM1 was introduced by Nitto Denko/Hydranautics (see below) to replace the CPA2 membrane wherever patent infringement considerations limited availability.

The performance of the CPA2 membrane was essentially equivalent to the FilmTec FT-30 membrane in terms of flux per unit area under brackish water test conditions, i.e. about 25 gfd. It exhibited a somewhat improved salt rejection, e.g. 98% minimum and 99% average NaCl rejection in spiral element form, tested on 0.2% NaCl solution. Comparative specifications for FilmTec® FT-30 spiral element products under similar test conditions were 96% minimum and 98% average NaCl rejection (although these specifications may be conservative).

A pair of patents issued to Tomaschke [146] and assigned to Hydranautics describe a method of making composite interfacial polyamide membranes utilizing an amine salt as an additive to the aqueous amine reactant solution. The acidic component of the salt may include, for example, hydrochloric acid, acetic acid, or a sulfonic acid. Amine components appear to be limited to tertiary amines and quaternary ammonium hydroxides, the latter being used with weak acids such as acetic acid. The triethylamine salt of camphorsulfonic acid appeared to be the best additive among those studied. In the experimental examples in the patents, a post-reaction drying operation at in excess of 100°C was employed. Membrane flux remained high despite this elevated temperature processing, implying that the amine salt ameliorated any heat-annealing effect on membrane flux. Salt rejections of the resulting membranes were very good, at 99.26 to 99.91%, measured on 2000 ppm NaCl solution at 225 psig. Permeate fluxes ranged from 15.1 to 22.3 gfd under these test conditions. One might speculate that the CPA2 and NTR-759 membranes were made according to the general method of these amine salt patents.

The specific function of the amine salt additive in the amine solution was not disclosed in the patents. The amine salts would not become a permanent part of the barrier layer. One possible role was as an inhibitor of any coalescing or fusing of the underlying polysulfone skin during the heat exposure processing step. A beneficial aspect of the amine salt additive is that this approach enables one to use a low flammability hydrocarbon solvent (such as Exxon's Isopar G, a high flash point petroleum distillate), which would require a high drying temperature for complete evaporative removal.

A generally equivalent effect to the amine salt is found in a patent by Chau et al. [147], assigned to Allied-Signal, Inc., which describes the preparation of a metaphenylene trimesamide membrane composition, wherein the freshly synthesized membrane is treated with citric acid, followed by drying at 100°C for 15 min. The acid treatment results in a finished membrane with high flux and rejection, whereas the untreated membrane loses most of its flux during the drying step, though maintaining high rejection. Thus, it appears that formation of an acid salt with residual amine groups after the interfacial polymerization step served the same function as having an amine salt present during the interfacial polymerization.

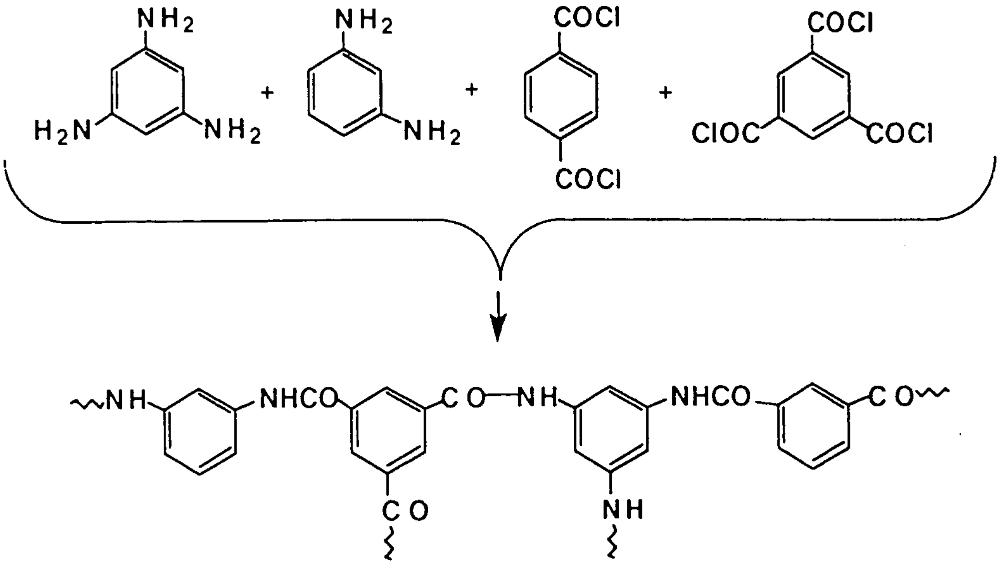
In technologically based countries where FT-30 patent coverage does not exist, membranes utilizing the basic FT-30 chemistry may be expected to come forth. One such example appears to be the Membrafil composite membrane line being developed by Ramot PuROtech Ltd. of Israel. While the compositions of these membranes have not been revealed, their performance properties strongly resemble the FT-30 membrane. Some improvement in organic rejections and capability of 99.6% seawater rejection are claimed in Membrafil product literature in side-by-side comparisons with FilmTec SW-30 membrane.

The UTC-70 membrane

Toray Industries developed a membrane designated as UTC-70, which is the basis of their SU-700 series of spiral element products. This membrane contains an aromatic polyamide barrier layer consisting of the product of a blend of diamine and triamine interfacially reacted with a blend of diacyl and triacyl halides. The diamine is 1,3-benzenediamine and the triamine appears to be 1,3,5-benzenetriamine. The triacyl halide is apparently trimesoyl chloride, and the diacyl halide, terephthaloyl chloride. The probable chemistry of the UTC-70 membrane is shown in Scheme 9.

This blend approach is described in a patent issued to Uemura et al. [142]. Flux and salt rejection performance are comparable to the CPA2/NTR-759 membranes. Performance data have been briefly described in Toray publications [95,148,149].

The 1,3,5-benzenetriamine monomer, if reacted solely with trimesoyl chloride, would have given so rigidly a crosslinked structure that the resulting barrier layer likely would have been too brittle. This is apparently mitigated by using difunctional intermediates in the reactant



Scheme 9.

blends. The partition coefficients of the triamine and the diamine are likely different, the triamine being potentially more water-bound. Thus, as mentioned earlier for the case of a 1,3-benzenediamine/piperazine blend, the final membrane composition would not necessarily duplicate the starting ratio of the aromatic amines in the aqueous solution. Nor, for that matter, has isophthaloyl or terephthaloyl chloride been proven to be equal in reactivity with trimesoyl chloride toward aromatic amines.

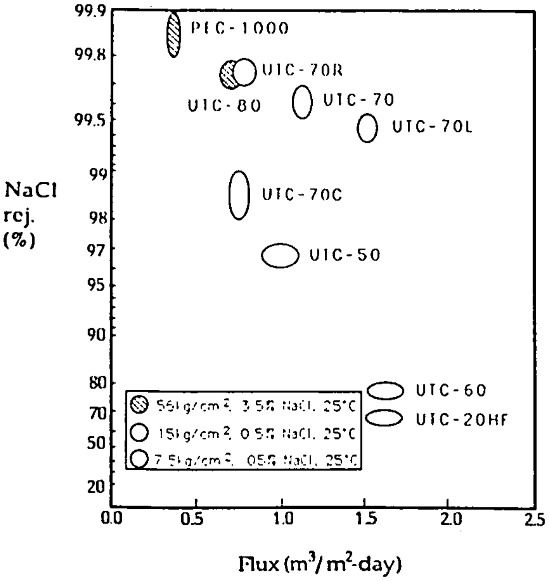


Fig. 11. Plot of rejection versus flux for the Toray UTC-70/80 crosslinked fully aromatic polyamide composite membranes versus other membranes [149].

Variations of the UTC-70 membrane are being developed for specific applications, especially in the area of ultrapure water production for semiconductor chip manufacturing [149]. In addition to the standard UTC-70 membrane, UTC-70C has been developed which shows superior rejection to trace levels of trimethylamine, a breakdown product of quaternized ion exchange resins used in ultrapure water polishing. And a UTC-70R membrane has been developed which exhibits improved rejections of low molecular weight organic compounds, and has application to wastewater recovery. Figure 11 shows, for example, the flux and salt rejection parameters of four such membranes intended for this industry. Besides the UTC-70 membrane products, new membranes designated UTC-80 and UTC-90 are being developed, which are also fully aromatic crosslinked polyamide composites. The UTC-80 membrane is intended for high pressure applications such as seawater desalination. The UTC-90 membrane appears to be intended for ultrapure water production in semiconductor chip manufacturing, where it is the second membrane in a two stage reverse osmosis system. It eliminates the need for an ion exchange resin deionization column.

As an example of a potential modified UTC membrane, a recent Toray patent application [150] described a membrane made from reaction of a 50/50 blend of trimesoyl chloride/terephthaloyl chloride with an aqueous solution containing 0.5% 1,3,5-benzenetriamine/1.5% 1,3-benzenediamine/0.4% N-methyl-piperazine, this membrane showing 99.2% NaCl rejection, tested on a 1500 ppm NaCl solution at 225 psig. The barrier layer in this membrane would be mildly basic (i.e. cationic) by reason of the tertiary amine residues arising from the N-methylpiperazine reactant. As such, it might be expected to have altered performance properties (e.g. pH of the permeate, rejections of amines). Other examples from Toray patent activity include use of 1,2-ethanediamine and of tetrafunctional aromatic amines with 1,3-benzenediamine in membrane formation, and use of tetraacyl halides or 4-chloroformyl phthalic anhydride in conjunction with trimesoyl chloride in the organic phase [151].

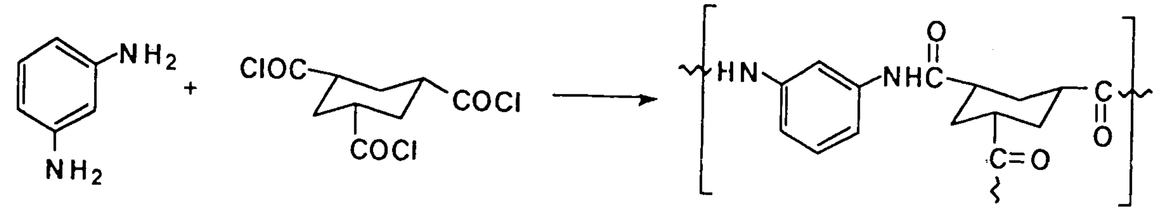
The A-15 membrane

Related to the FT-30 membrane chemistry is the Permasep A-15 composite polyamide membrane originally developed by Sundet and coworkers [152] at DuPont, but now owned by Trisep Separations. This membrane has also been called the ACM *a*dvanced *c*omposite *m*embrane. The barrier layer of this membrane is the reaction product of 1,3-benzenediamine with cyclohexane-1,3,5-tricarbonyl chloride, the latter being the saturated analog of trimesoyl chloride. It is therefore an aralkyl polyamide as distinguished from the fully aromatic structures of FT-30, CPA2 and UTC-70. The chemistry of the membrane may be shown in Scheme 10.

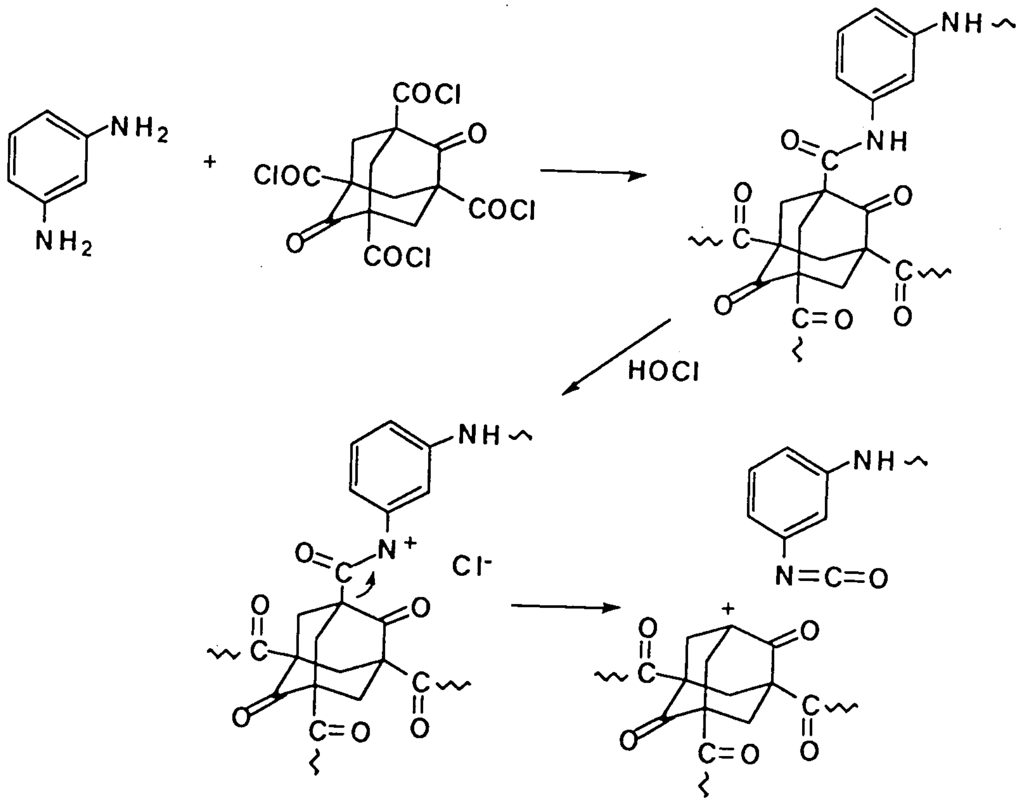
A series of patents [153] have issued covering various aspects of formulation and fabrication of this composite membrane, including for example the use of acyl halide blends, and also of quenching the polysulfone support layer in an aqueous 1,3-benzene-diamine solution for higher flux membranes. The cyclohexane-1,3,5-tricarbonyl chloride appears to give a higher ratio of carboxylate content than trimesoyl chloride. This results in higher flux membranes but with lower salt rejections relative to the fully aromatic composites. Arthur [154] compared membranes made with trimesoyl chloride, its cyclohexane analog, and also adamantane-2,6-dione-1,3,5,7-tetracarbonyl chloride, each one interfacially reacted with 1,3-benzenediamine. Both the cyclohexane (HT) and adamantane (ADTC) membrane analogs showed higher water flux than the trimesoyl chloride (TMC) analog, but at lesser salt rejection levels: TMC, 99%; HT, 98%; ADTC, 97%, measured on 0.2% NaCl solution at 420 psig. Equilibrium water absorption levels, measured at 95 to 100% relative humidity, were 39.6% for the TMC polyamide, 56% for the HT analog, and 65.8% for the ADTC analog, showing a general correlation with membrane flux. Increased content of carboxylic acid content in the respective polyamides accounted for some, but not all of the increased water absorption.

The ADTC membrane analog showed the least resistance to chlorine attack despite a greater degree of crosslinking. Possible mechanisms of chlorine attachment and chain cleavage of the ADTC polyamide were postulated as shown in Scheme 11.

Use of a tetraacyl halide derived from 2,3,4,5-furan-tetracarboxylic acid has also been de-



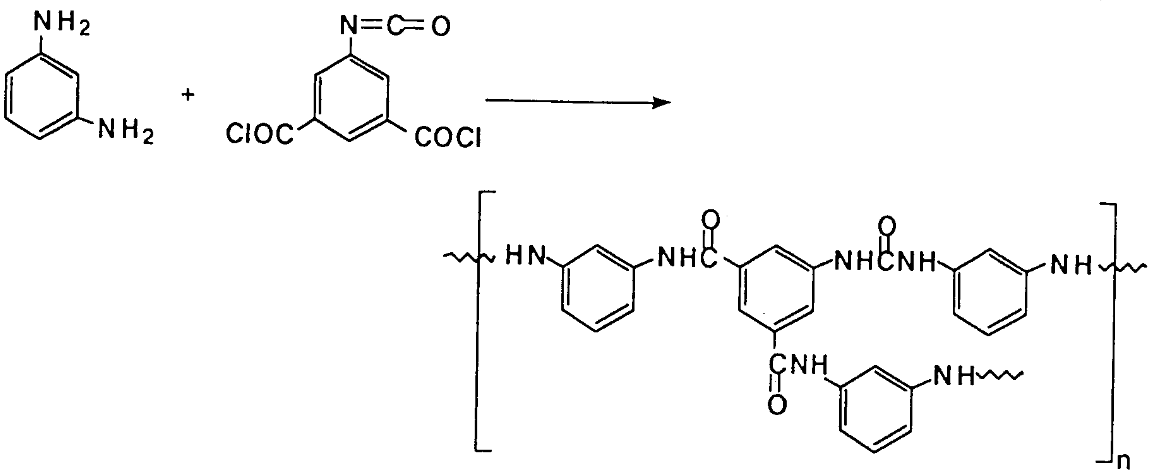
Scheme 10.



Scheme 11.

scribed in one of Sundet's patents [155].

A new, potentially important development is the use of isocyanato aromatic acyl halides in interfacial composite membranes, as described in a recent Sundet patent [156]. In essence, the carbonyl chloride groups of trimesoyl chloride can be sequentially replaced with isocyanate groups, generating useful membranes via interfacial polymerizations with aromatic amines. Best results were achieved for a composite membrane made from 1,3-benzenediamine interfacially reacted with 1-isocyanato-3,5-benzenedicarbonyl chloride (i.e. 5-isocyanato-isophthaloyl chloride), which produces a barrier layer containing both amide and urea linkages. A membrane with 99.33% rejection at 24.8 gfd was obtained, tested under conditions of 0.2% NaCl at 225 psig. An idealized chemistry of the



Scheme 12.

barrier layer may be shown as follows (Scheme 12).

Relative reactivities of the isocyanate versus carbonyl chloride moieties was not discussed in the patents. It is not known whether their reactivity differences play an important role in membrane formation and performance. The rights to the use of the isocyanato acyl halide reactants in this composite membrane technology are believed to be part of the technology acquired from DuPont by Trisep Separations.

The NCM1 membrane

When the CPA2 membrane of Hydranautics was removed from the U.S. commercial marketplace by a patent infringement judgement, a new composite membrane, NCM1, was rapidly brought to the marketplace by Hydranautics and its parent company, Nitto Denko. The specific chemical composition of the NCM1 membrane has not been publicly revealed. The membrane has been described, however, as a thin film composite polyamide polymer on a polysulfone support, developed in part with the assistance of computerized molecular structure imaging [157]. Product literature lists NaCl average rejection as 99%, tested on 1500 ppm NaCl solution at 225 psig and 25°C. Listed spiral element flux data appear to correspond to a membrane flux of approximately 30 gfd under the 225 psig test condition.

Composite membranes having sulfonated compositions: the NS-200 and PEC-1000 membranes

Sulfonic acid groups are highly hydrophilic, and may help to produce good flux in compositions not otherwise noted for water permeability. Asymmetric membranes made from sulfonated polyphenylene oxide, i.e. poly(2,6-dimethyl-1,4-phenylene-oxy), were known in the 1960s. A method was also developed for dip-coating a solution of this sulfonated polymer onto microporous polysulfone from a solution blend of nitromethane, methanol and butanol [158,159]. Research was undertaken on sulfonated composite membrane compositions at North Star Research Institute in 1971, leading directly to the NS-200 membrane, and perhaps indirectly to sulfonated polysulfone composite products.

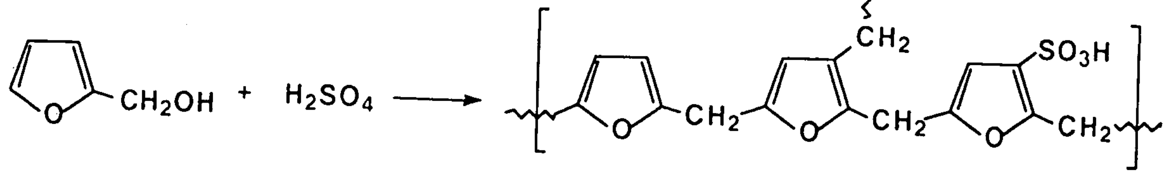
The NS-200 membrane was discovered by Cadotte [160], and optimized by Cadotte and his co-workers [161]. It consisted of a sulfonated polyfurane barrier layer formed in place on (and in) the surface of a porous polysulfone support. A dip-coating method of application was used. The polysulfone support was coated with an aqueous solution containing furfuryl alcohol and sulfuric acid. The coated support was then heated in an air oven at 125 to 140°C for 15 min. The furfuryl alcohol was polymerized to a dark brown to black resin, being simultaneously sulfonated. The resulting membrane showed extremely good salt rejections in short term seawater tests, typically showing 99.8 to 99.9% salt rejection. Fluxes were generally about 20 gfd in the 1500 psig synthetic seawater test, but occasionally fluxes of as high as 40 to 50 gfd were seen.

Furfuryl alcohol polymerizes to polyfurane resins in solution, even at room temperature, in the presence of a strong acid such as sulfuric acid. The resin content exceeds its water solubility in the time of about 15 min. Solution potlife can be extended to a few hours by use of isopropanol as a co-solvent. Various additives were examined as potential flux-promoting agents, such as polyols, sugars, carboxylic acids, and water-soluble resins. Best results were obtained with a nominally 20,000 molecular weight polyethylene oxide. An optimized dipcoating recipe consisted of 2% furfuryl alcohol, 2% sulfuric acid, and 1% Carbowax 20M (Union Carbide) polyethylene oxide dissolved in an 80:20 blend of water:isopropanol.

The NS-200 membrane surface was nearly a glossy black when freshly prepared, but turned brown when wet. The barrier layer chemistry in its early stage of polymerization might be projected as shown in Scheme 13.

The ultimate composition of the barrier layer showed no similarity at all to a simple polyfuran resin. Rather, a tightly crosslinked, highly unsaturated, sulfonated barrier layer was generated. About 0.05 meq of sulfonic acid groups was present per gram of barrier resin. Water absorption was low at less than 2%, measured at 75% relative humidity.

The dark color was attributed to a high degree of conjugated unsaturation in the barrier layer. The barrier layer was partially decolorized by a few days exposure to sunlight, with an attendant decline in salt rejection. The membrane performance was also drastically harmed by exposure to chlorinated water. Long term seawater tests (1000 hr tests) showed a significant fall-off of salt rejections with time, which could be mostly prevented by periodic treatment of the NS-200 membrane with a multivalent cation. Barium ion worked best. Another factor believed to affect NS-200 membrane instability was hydrolysis of sulfate and sulfonate esters possibly present in the sulfonated polyfurane resin matrix, leading to swelling of the barrier layer. One means of evaluating the stability of an NS-200 membrane formulation was to soak the resulting membrane in an ammonium hydroxide solution before testing. This brought forward any hydrolytic instability. It was not fully realized until the later development of the PEC-1000 membrane by Toray Industries that degradation of



Scheme 13.

the NS-200 membrane by dissolved oxygen in the feedwater was a significant contributing factor in salt rejection loss.

Because of the excellent seawater rejection data observed for freshly prepared NS-200 membranes, a major effort was invested by several membrane companies to develop a commercial version of the membrane [162–164]. Results by others included seawater salt rejections of up to 99.6% at a flux of 23 gfd, tested at 800 psig, and brackish water fluxes of up to 50 gfd at 98% NaCl rejection, tested on 0.5% NaCl solution at 250 psig. These efforts did not culminate in stable commercial membranes, however. This remained to be achieved by Toray Industries in a membrane designated PEC-1000.

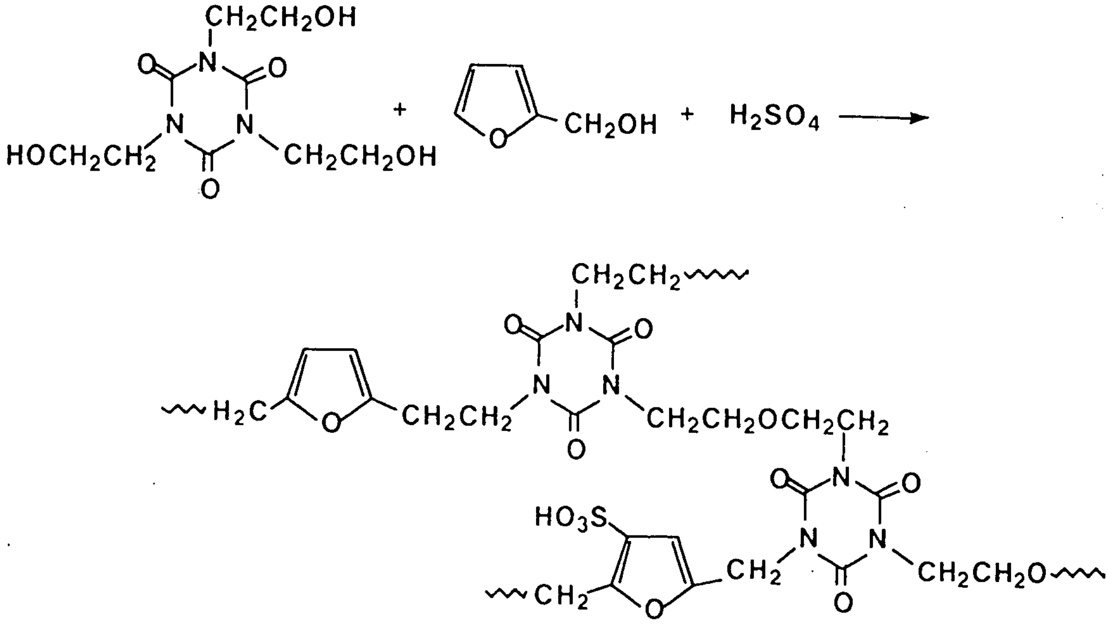
The PEC-1000 membrane has been described by Kurihara and co-workers [165,166]. It was prepared by an acid-catalyzed condensation reaction *in situ* on a microporous polysulfone support, and contained a barrier layer estimated at about 300 Å thick. The composition was not publicly stated, but it was covered by a U.S. patent that described acid-catalyzed compositions based on 1,3,5-tris(hydroxyethyl)isocyanuric acid (THEIC) [167]. This monomer was condensed with co-reactants such as sorbitol or polyethylene glycol, giving membranes with 95 to 97% NaCl rejection (0.25% NaCl at 570 psig) and excellent organics rejections. Water fluxes were very low.

However, when THEIC was co-condensed with furfuryl alcohol, fluxes were tenfold higher, and the extremely high salt rejections characteristic of NS-200 were obtained. Organic solute rejections remained high as well. A typical preparation according to the patent employed an aqueous dip-coating solution containing 1% THEIC, 2% furfuryl alcohol, 2% sulfuric acid and 1% dodecyl sodium sulfate, coated onto polysulfone and heat-cured at 150°C. This formulation showed 99.9% seawater salt rejection and 12 gfd water flux, tested at 1000 psig. No other commercial reverse osmosis membrane is known to have matched this seawater 99.9% rejection performance level to date.

The chemical structure of the membrane barrier layer would obviously be quite complex, involving polyether formation between THEIC moieties along with polyfurane formation. Early stage oligomerization could involve the following types of linkage shown in Scheme 14.

This membrane was fully capable of single-pass seawater desalination, even on high salinity feedwaters such as in the Persian Gulf (42,000 ppm). Performance results on PEC-1000 spiral wound modules at a seawater test facility in Toray's Ehime plant, under conditions that simulated Red Sea salinities, have been reported in the literature [168]. Because of its sensitivity to dissolved oxygen, the PEC-1000 membrane was protected in small installations by the addition of bisulfite ion to the feedwater. In large installations, barometric degasification of the feedwater was used in plant design. Figure 12, taken from a paper on PEC-1000 membrane transport characteristics by Chen et al. [169], shows the position of the PEC-1000 membrane in the hierarchy of reverse osmosis membranes considered for seawater desalination back in 1983.

Regarding rejections of organic compounds, the PEC-1000 membrane was unexcelled. Rejections of small, water-soluble organic compounds, measured at 4 to 5% feed concentrations in most cases, typically exceeded 95%. Ohya and co-workers have published several articles comparing the performance of the PEC-1000 membrane to other membranes for the concentration of urea [170], N,N-dimethylformamide [171], N,N-dimethylacetamide [172], ε-caprolactam [173], alcohols [174], and several other small organic molecules [175,176]. Figure 13 illustrates its performance relative to a few other prominent reverse osmosis membrane types in terms of rejection of selected or-



Scheme 14.

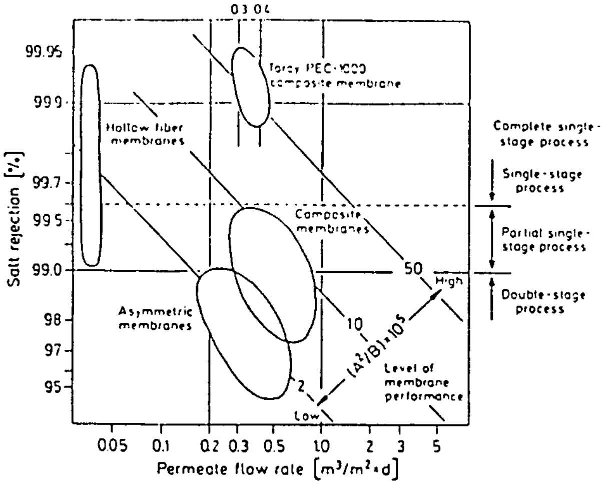


Fig. 12. Position of the PEC-1000 membrane versus other reverse osmosis membranes in relation to single-stage seawater desalination capabilities [169].

ganic compounds, arranged according to their rejection by cellulose acetate.

The PEC-1000 membrane has reportedly been withdrawn from production [177]. The commercial potential of this membrane appears to have been overshadowed by its sensitivity to oxidants, by the continued hold of market share by hollow fiber modules (DuPont and Toyobo) in the Middle East, and by the success of FT-30 seawater spiral modules elsewhere.

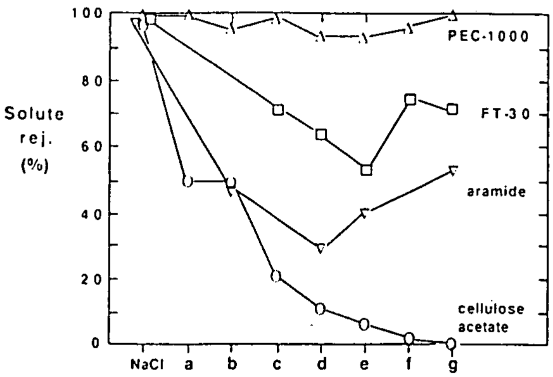


Fig. 13. Organic rejection data for the PEC-1000 membrane compared to FT-30, asymmetric aramide and asymmetric cellulose acetate membranes (a) caprolactam, (b) ethylene glycol, (c) acetone, (d) ethanol, (e) acetic acid, (f) aniline, (g) phenol [1].

Activity on compositions duplicating or closely following the PEC-1000 composition continue on by others. A Chinese group has reported on a composite membrane, designated as the PFT membrane [178], which is made from the condensation product of furfuryl alcohol with THEIC. Salt rejections were not as high as for the PEC-1000 membrane. This same group has reported on a PFI composite membrane [179], which may be the same as, or closely related to, the PFT membrane. Wang [180,181] has reported on composite membranes wherein the barrier layer is formed by acid-catalyzed condensation of tris-hydroxymethyl-melamine with furfuryl alcohol. A salt rejection of 95%, tested against a 1500 ppm NaCl solution, was observed, which decreased to about 92% in contact with 30 ppm hydrogen peroxide over a period of 100 hr exposure time. Sumitomo Chemical Co. filed a patent application covering the preparation of a composite membrane in which pentaerythritol was co-condensed with furfuryl alcohol in the presence of sulfuric acid [182].

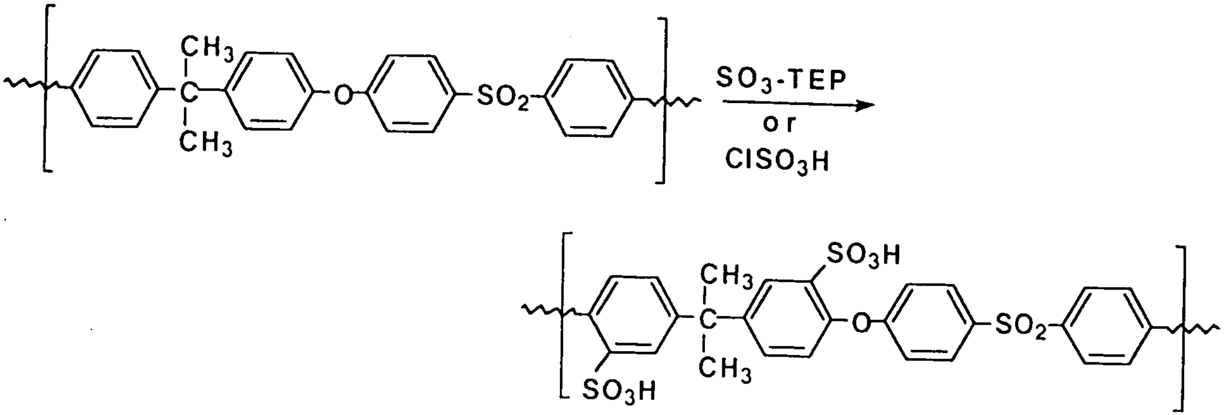
Sulfonated polysulfone membranes

Asymmetric membranes composed of sulfonated polysulfone have been reported in patents by Rhône-Poulenc in 1973 and after [183,184]. A characteristic of such membranes is that an increasing degree of sulfonation correlates with increasing flux and falling salt rejections. The cross-over point for these two effects has generally been unfavorable in these asymmetric membranes, that is, salt rejections fell below a commercially practical level by the time sulfonation-induced flux reached the desired level.

Cadotte and co-workers [76] experimented with composite sulfonated polysulfone membranes, using an approach wherein a water-soluble grade was prepared, then coated and heat-cured on the surface of a polysulfone support. Polysulfone, having both a diphenylsulfone group and a bisphenol-A group (i.e. 2,2-diphenyl-propylidene group) in the polymer backbone, can be selectively sulfonated on the two rings of the bisphenol-A group by a reagent such as sulfur trioxide/triethyl phosphate complex or chlorosulfonic acid, as shown below. Partial sulfonation of the diphenylsulfone group can also occur with chlorosulfonic acid when this reagent is used in excess. The degree of sulfonation of polysulfone rings is controllable by varying the amount of chlorosulfonic acid used, thereby generating differing grades of hydrophilicity (Scheme 15).

Various grades of sulfonated polysulfones made in this manner were dissolved in water or aqueous alcohol blends, were coated onto polysulfone supports, then heat-cured at temperatures of 100 to 140°C. The sulfonated polysulfone was insolubilized at these temperatures. The mechanism of insolubilization has not been definitively determined; intramolecular sulfonation may be involved. Crosslinking can be increased via additives such as polyols or polyphenols which are reactive with the sulfonic acid groups. Various membrane examples were produced that showed high rejections of NaCl in tests on dilute solutions such as 0.1% NaCl. Salt rejections were much lower when salinities were increased. A typical value for a seawater feed, for example, was 80% or less salt rejection.

Researchers at Albany International Corporation had worked on a composite hollow fiber version of the NS-200 membrane with some limited success [164]. Their efforts were subsequently re-directed to sulfonated polysulfone composites for brackish water treatment, with more promising results [185,186]. They developed a composite hollow fiber membrane that exhibited 98% salt rejection and 1 gfd in a 5000 hr test at 400 psig on 3500 ppm brackish water (simulated agricultural drainage water). Flux and salt rejection were unaffected by exposure to chlorine in this test, even when the chlorine



Scheme 15.

exposure level was increased to 100 ppm. Another version of this membrane, tested on actual seawater at 1000 psig for 12,000 hr, showed better than 98% salt rejection at an average flux of 1.5 gfd (a reasonable membrane flux for a hollow fiber reverse osmosis module).

Rights to this membrane technology for certain applications were sold to Millipore Corporation, who encountered difficulty in developing it into a commercial product. However, Millipore Corporation did succeed in developing a flat sheet and spiral-wound module version of a sulfonated polysulfone composite reverse osmosis membrane with excellent flux. The membrane was originally designated as the PSRO membrane, and a line of spiral modules designated as Hi-Flux CP® was developed incorporating this membrane. Rights to this membrane were acquired from Millipore by Eastern Enterprises, and are now owned by their Ionpure Technologies unit.

Allegrezza and co-workers [187–189] have reported on the performance properties of modules made with this sulfonated polysulfone membrane. The membrane combines three favorable performance features: high chlorine resistance, high flux, and good salt rejections to monovalent salts in dilute solutions. Figure 14 shows the behavior of this membrane toward dilute sodium chloride solutions at different operating pressures. Salt passage decreases dramatically with decreasing salinity and increasing operating pressure (higher permeate flux), thus showing a very strong Donnan ion repulsion effect. Salt rejection is adversely impacted by small amounts of divalent cations, as evidenced by the data in Table 8 for blends of sodium and calcium chlorides. Calcium is know to be an effective shielding agent toward charged sites in a Donnan dialysis membrane. This membrane appears to operate best under conditions of a sufficiently high transmembrane pressure to generate permeate fluxes that are higher than normally acceptable in reverse

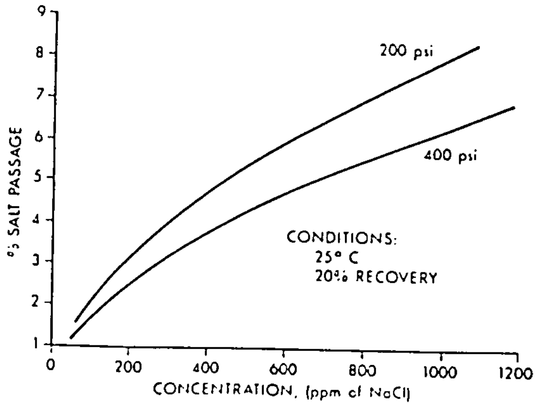


Fig. 14. Sodium chloride passage as a function of pressure and NaCl concentration for a sulfonated polysulfone reverse osmosis membrane [187].

TABLE 8

Effect of cationic mixture on the cation and conductivity rejection of a sulfonated polysulfone membrane.

Feedwater mixture (ppm)		Rejection data (%)		
Na^+	Ca^{2+}	Na^+	Ca^{2+}	Conductivity
126	0	97	-	97
122	8	94.4	100	95.6
136	6	92.6	98.8	94.4
138	50	90.6	98.6	93.1
140	104	84.2	98.0	91.5
0	8	-	92.3	92.3
0	32	-	91.0	91.0
0	100	-	88.7	88.7

osmosis installations. Abnormally high fluxes correlate with enhanced membrane fouling. However, the superior fouling resistance of the sulfonated polysulfone membrane appears to enable high flux operation. Application would be generally limited to very low salinity feedwaters.

A natural application for this membrane is as a first stage water treatment before a de-ionization column in the preparation of a high purity water from a soft (or softened) tapwater source. The principal disadvantage of the PSRO membrane is its low salt rejection when the feed contains divalent cations. The dependence mechanism of salt rejection on Donnan ion repulsion suffers from the fact that divalent cations such as calcium ions have a strong ion shielding effect.

TABLE 9

Reverse osmosis performance data for the NTR-7400 series sulfonated polysulfone membranes

	NTR-7410	NTR-7450	Cellulose acetate	
			Loose	Tight
Flux (m^3/m^2-day)	12	2.2	2.0	1.0
Pressure (MPa)	1.0	1.0	1.0	1.4
Solute				
NaCl	15	51	11	54
Na_2SO_4	55	92	33	96
$MgCl_2$	4	13	20	80
$MgSO_4$	9	32	41	92
Sucrose	5	36	35	85
Dye (300 *MW*)	98	100	-	-
Aspartic acid (pH 2)	0	20	-	-
Aspartic acid (pH 12)	80	98	-	-

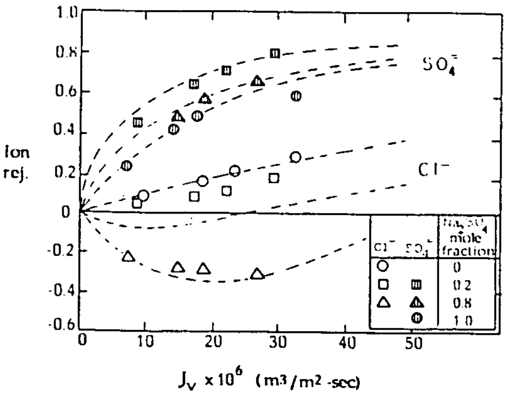


Fig. 15. Salt rejection data on mixed chloride/sulfate solutions showing negative rejection of the more permeable anion through the NTR-7410 membrane (lines are calculated from theory) [192].

Nitto Denko has itself produced commercial composite sulfonated polysulfone membranes under the NTR-7400 series designation [190,191]. These are more characteristic of older sulfonated polysulfone compositions, exhibiting high fluxes but with low salt rejections. Data for the NTR-7400 membrane are shown in Table 9. Tsuru and co-workers [192,193] have examined the behavior of these membranes toward feed solutions containing mixed electrolytes. One phenomenon observed with loose, charged membranes of this type is the negative rejection of an anion in mixed salt solutions, i.e. the permeate is enriched in a particular anion relative to the feedstream. Figure 15, for example, shows that negative rejection of chloride ion can occur in mixed sulfate/chloride feed solutions with an NTR-7410 membrane sample [192].

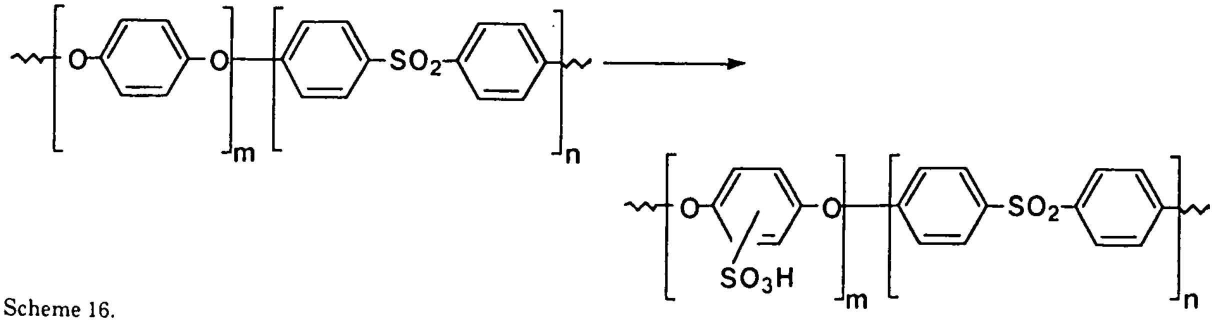
Patent activity by Nitto Denko in the area of thin film composite sulfonated polysulfone membranes centered on a composition in which hydroquinone moieties were copolymerized with 4,4′-bis-hydroxyphenylsulfone into a polyether sulfone. All the hydroquinone moieties were subsequently sulfonated, generating the type of chemistry shown below [194–196]. The ion exchange capacity of the resulting polymers was controlled by controlling the amount of hydroquinone incorporated into the polyethersulfone (Scheme 16)

Sulfonated compositions with 1.92 meq/g of ion exchange capacity, applied as 3000 Å films on porous polysulfone supports, showed 35 to 50% NaCl rejections, tested on 5000 ppm NaCl solution at 50 kg/cm^2. Water fluxes to 5.9 m^3/m^2-day were observed at this high operating pressure. A composition with 1.23 meq/g exhibited 98.6% rejection under the same test conditions, though most likely at low flux.

Desalination Systems, Inc., manufactures a series of ultrafiltration membranes under a G-series designation, wherein microporous polysulfone supports appear to be surface-coated with a sulfonated polysulfone composition. No description of their composition is found in the technical or patent literature. The surface coating improves the fouling resistance of the polysulfone ultrafilters, and may be presumed to play a role in molecular weight cutoff as well. For comparison, Advanced Membrane Technology, Inc., has a sulfonated polysulfone composite membrane with performance basically equivalent to the G-10 membrane of Desalination Systems. The AMT membrane, designated as ASP-35, has a water flux of 30 to 40 gfd, 30 to 40% NaCl rejection and 45 to 55% lactose rejection, tested at 225 psig on 2,000 ppm feed solutions.

Desalination Systems also manufactures composite membranes with nanofiltration and reverse osmosis rejection characteristics. One example is the Desal-5 membrane with performance akin to a very good NS-300 membrane. Another example is the Desal Plus membrane with performance approximating the brackish water version of FilmTec's FT-30 membrane.

The composition of the Desal-5 membrane has not been publicly revealed, and no patent activity by Desalination Systems points toward a possible composition. The membrane is negatively charged and displays Donnan ion exclusion behavior toward inorganic ions in aqueous feed solutions [197]. However, the performance characteristics are different than for sulfonated polysulfone membranes such as made by Ionpure Technologies or Nitto Denko. The Desal-5 membrane appears to consist of a three layer composite: microporous polysulfone, sulfonated polysulfone overlay (i.e. interlayer), and an additional, highly ultrathin barrier layer (polypiperazineamide ?) built upon the sulfonated polysulfone layer. This description is admittedly speculative. Similarly, the



Scheme 16.

TABLE 10

Organic rejection characteristics of the Desal-5 membrane

Substance	Molec. weight	Rejection (%)
Methanol	32	2
Ethanol	46	2.5
n-Butanol	74	8
Diethylene glycol	124	25
Triethylene glycol	186	52
Glucose	180	82
Sucrose	342	99
Lactose	342	99

Desal Plus membrane may possibly consist of a highly ultrathin aromatic polyamide built onto a sulfonated polysulfone interlayer.

Table 10 contains organic compound rejection data on the Desal-5 membrane [197]. Of particular note is the 99% rejection of lactose. This membrane has found widespread application in cheese whey concentration because of its ability to retain lactose and other BOD-generating organic compounds, while passing a significant portion of the inorganic salts (principally NaCl) contained in the whey.

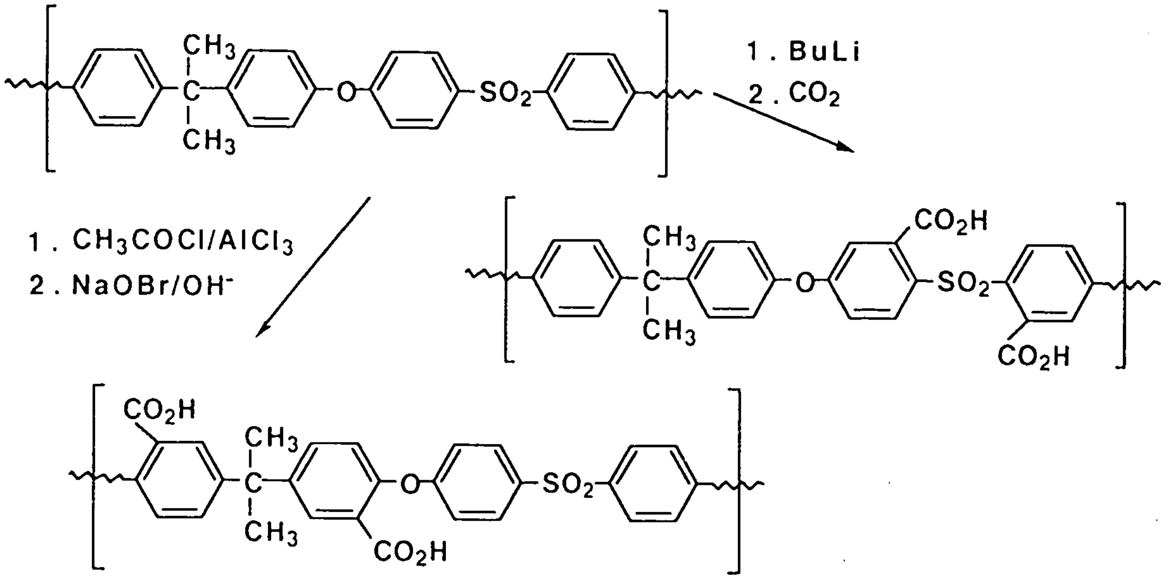
Sulfonated polyphenyleneoxide

In the introductory remarks on the NS-200 membrane, mention was made of early work on sulfonated polyphenylene oxide as a reverse osmosis membrane material. In the mid-1980s, some interest in this material as a barrier layer in thin film composite membranes reappeared. Agarwal and Huang [198,199] prepared composite membranes of sulfonated polyphenylene oxide on polysulfone, using grades with 2.14 and 2.50 meq/g of ion exchange capacity. These composite membranes were treated with various acids, bases, and gamma irradiation in an effort to enhance performance properties. In the area of patent activity, Kubota and Yanase [200] synthesized a sulfonated polyphenylene oxide sample with 2.2 meq/g of ion exchange capacity, prepared solutions in either methanol or 2-butoxyethanol (butyl cellosolve), and coated them onto microporous polysulfone hollow fibers. The composite from the 2-butoxyethanol solution showed a flux of 1.01 m^3/m^2-day and 90% rejection of β-cyclodextrin. The methanol solution example showed high flux and high leakage of the β-cyclodextrin.

Carboxylated polysulfone and polyphenylene oxide

Attaching the highly hydrophilic sulfonic acid group to otherwise hydrophobic polymers, such as polysulfone and polyphenylene oxide, has involved a balancing act: achieving economical water fluxes versus maintaining attractive salt rejections. If one were to instead derivatize these polymers with carboxylic acid groups, perhaps the cross-over point of flux versus salt rejection might be shifted favorably for reverse osmosis applications. This has indeed been tried.

Guiver and co-workers [201,202] prepared carboxylated polysulfone by lithiation of Udel P-1700 polymer in tetrahydrofuran, followed by carbonation. NMR analysis of the methyl ester form of the resulting polymer showed the carboxyl substitution to be *ortho* to the sulfone linkage. Carboxylated polysulfone with 0.62 acid group per polymer repeat unit was formed into asymmetric membranes (rather than into thin film composite membranes) for reverse osmosis tests. Salt rejections of about 93% at permeate fluxes of 0.5 m^3/m^2-day were attained, tested at 500 psig on a 3500 ppm NaCl solution. Himeshima and Kurihara [203] carboxylated Udel P-1700 and P-3500 by a different route that put the carboxylic acid groups on the bisphenol-A rings. The polysulfone was reacted with acetyl chloride in the presence of aluminum chloride to place acetyl groups on the aromatic rings. These were converted to carboxylic acid groups by a haloform reaction method.



Scheme 17.

The chemistry of the above two routes is shown in Scheme 17.

Asymmetric membranes were cast from the polymers. Neither of the two groups have apparently reported any efforts to make composite membranes of these compositions.

Poly(vinyl alcohol)-based composite membranes

Poly(vinyl alcohol), by virtue of its hydrophilic nature, is a useful building block in reverse osmosis membranes. It has found application in the poly(piperazineamide) membranes as described earlier. It is also commonly used as a protective surface coating on the top of composite membranes. Here, its purpose is to enable one to handle and fabricate the membranes into spiral-wound elements without causing damage to the ultrathin barrier layer. Poly(vinyl alcohol) should also be a useful material for a desalinizing barrier layer, based on its hydrophilic character and its reactivity toward crosslinking reagents. Indeed, poly(vinyl alcohol) has been used in that way.

She and Shen [204] listed in a table the published activity by others over the period 1961 to 1984 on reverse osmosis membranes made with poly(vinyl alcohol). They themselves coated a microporous polysulfone support with an aqueous poly(vinyl alcohol) solution, doped the poly(vinyl alcohol) coating with a combination of sulfuric acid and an organic polycarboxylic acid, then heated the composite film to 90 to 120°C to crosslink the poly(vinyl alcohol) via ester linkages. Polycarboxylic acids that were tried included oxalic acid, malonic acid, succinic acid and citric acid. Of these, best results were achieved with oxalic acid, whereby a membrane with about 95% salt rejection was attained, tested on 0.35% NaCl solution at 40 kg/cm^2. Permeate flux was very low, however, at less than 2 gfd for this example.

Cadotte [33] also explored the use of polyvinyl alcohol in composite membranes, using aldehydes as crosslinking agents. He first coated an emulsion of polyvinyl acetate doped with sulfuric acid and formaldehyde onto a polysulfone support, heating to 110°C to cause hydrolysis of the acetate groups with concomitant crosslinking by formal linkages. This membrane exhibited a permeate flux of 21 gfd at 90% salt rejection, tested on synthetic seawater at 1500 psig. Using poly(vinyl alcohol) solutions instead gave either high flux membranes with low salt rejections, or low flux membranes with only moderate salt rejections at best. Comparatively good data for flux and salt rejection were obtained by crosslinking poly(vinyl alcohol) with acrolein, employing the acrolein in the form of its bisulfite salt. Thus, Cadotte refluxed an aqueous solution of 2:2:1 wt% poly(vinyl alcohol):acrolein:sodium sulfite, ostensibly to force addition of the hydroxyl groups across the active double bond of the acrolein. Sulfuric acid was then added, the solution was coated onto a polysulfone support. It was then cured at 135°C for 15 min to form acetal linkages. Membranes formed by this procedure exhibited fluxes of 18 to 21 gfd at 96.5 to 96.7% salt rejection in 1500 psig tests on synthetic seawater. Fluxes were raised to the range of 24 to 31 gfd at equivalent salt rejections by diluting the coating solution. Pre-reacting the poly(vinyl alcohol) with propanesultone, followed by acid-catalyzed crosslinking with formaldehyde provided membranes with only 70 to 82% salt rejection (fluxes of 18 to 46 gfd) under the same test conditions.

A drawback stated by Cadotte relative to poly(vinyl alcohol) membranes was the flexibility of the polymer backbone and its propensity toward compaction under high operating pressures, although this comment was related to the goal of seawater desalination membranes. Fujimaki et al. [205] prepared thin film composite membranes from poly(vinyl alcohol) by crosslinking with inositol (i.e. hexahydroxycyclohexane) and sulfuric acid. A solution of 0.2% poly(vinyl alcohol) (78% hydrolyzed) was doped with 3% inositol and 3% sulfuric acid, coated onto polysulfone, and heated at 120°C for 10 min. The resulting membrane, tested at 20 kg/cm^2 on 0.2% $MgSO_4$ solution, showed 99.5% $MgSO_4$ rejection and 1.1 m^3/m^2-day permeate flux. Later, Himeshima and Uemura [206] prepared a poly(vinyl alcohol) composite membrane by crosslinking the poly(vinyl alcohol) with divinyl sulfone at 70°C under alkaline conditions. This membrane exhibited 15% NaCl rejection, tested on 1500 ppm NaCl solution at 7.5 kg/cm^2. A good permeate flux of 0.33 m^3/m^2-day was observed, even at this very low test pressure (about 107 psig).

Cadotte [207] prepared a version of a poly(vinyl alcohol) composite membrane wherein the polymer was crosslinked by acetalization with a dialdehyde, catalyzed by phosphoric acid at about a 100 to 110°C heat-cure. An excess of phosphoric acid was used in the formulation, and served simultaneously as a catalyst and as a pore-former. Thus, permeate flux increased as a function of the level of phosphoric acid employed in the coating formulation. The excess phosphoric acid washed out upon contact with water in a reverse osmosis operation. Membranes made in this way exhibited about 17% NaCl rejection and 29 gfd (tested on 0.2% NaCl at 200 psig and 25°C), and about 80% sodium EDTA rejection and 25 gfd (tested on 0.2% Na_4EDTA solution at 200 psig and 25°C). Sulfuric acid could be added as a co-catalyst, but generated tighter membranes with NaCl rejections of 35% and higher. The membranes exhibited molecular weight cutoffs in the range of 500 and higher, and were useful for desalting of solutions of middle molecular weight organic compounds. High stability to alkali exposure was also noted. An experimental membrane generally meeting these performance characteristics was reported on by Cadotte and co-workers [91]. Designated as XP-20, it was listed as having a NaCl rejection of 20%, a $MgSO_4$ rejection of 85%, a 99% rejection of copper-EDTA complex, and essentially zero rejection of sodium nitrate. Net driving pressure to generate 20 gfd was 150 psig. Application was seen for concentration of copper–EDTA chelate in alkaline electroless plating baths.

Potential nanofiltration applications were briefly summarized by Rautenbach and Gröschl [208] for a variety of commercial nanofiltration membranes, including the XP-20, NF-40, Desal 5, SU-600 and NTR-7400 membranes.

The NTR-729HF and NTR-739HF membranes

Two composite membranes with significant chlorine resistance, NTR-729HF and NTR-739HF, have been commercialized by Nitto Denko for use in desalinating low salinity brackish waters [209,210]. These membranes have particularly found use in the preparation of ultrapure water for the semiconductor industry. The NTR-729HF and NTR-739HF membranes have been commonly referred to as poly(vinyl alcohol) membranes [177,211,212] in the membrane literature. This is probably a misnomer. Infrared spectra of the barrier layers of NTR-729HF and NTR-7250, for example, are almost identical; that is, both show polyamide to make up a major proportion of the barrier layer, the polyamide appearing to be a poly(piperazineamide). Poly(vinyl alcohol) is also present in both barrier layers, though more so in the NTR-729HF barrier layer. The NTR-739HF also appears to be a polyamide/poly(vinyl alcohol) composition, but not a poly(piperazineamide) [95]. Examination of the patent activity of Nitto Denko does not reveal work on poly(vinyl alcohol) as a sole membrane matrix. Rather, combinations of poly(vinyl alcohol) and diamines, interfacially reacted with acyl halides, were commonly described in Nitto Denko patent applications [213–215].

One of these patent applications [213] describes a way a making a composite membrane of poly(vinyl alcohol)/poly(piperazineamide) wherein the membrane is irradiated in a post-treatment step to increase the degree of cross-linking. For example, a polysulfone support was coated with an aqueous solution containing 0.25% poly(vinyl alcohol), 0.25% N,N′-dimethyl-1,2-ethanediamine, and 0.5% sodium hydroxide. This was then dipped into a hexane solution of 1.0% trimesoyl chloride for one minute. The interfacial polyamide/ester was then heated to 110°C (to insolubilize unreacted poly(vinyl alcohol)), followed by 10 Mrad of irradiation with an electron beam. The resulting membrane exhibited 0.98 m^3/m^2-day flux and 98.2% $MgSO_4$ rejection, tested on a 500 ppm $MgSO_4$ solution at 10 kg/cm^2 and 25°C. The irradiation step stabilized the membrane to chemical attack, such that it withstood exposure to two weeks in 100 ppm chlorine solution, one month in pH 1 and 12 solutions, and one month in 80°C water. Other secondary amines such as piperazine could be used. One or both of the NTR-729HF and NTR-739HF membranes may very possibly be irradiated preparations such as described in this patent.

Table 11 lists some solute rejection data for these membranes compared to cellulose acetate.

Figure 16 shows the position of these two

TABLE 11

Solute rejection data for NTR-729HF and NTR-739HF membranes

Solute	NTR-729HF (%)	NTR-739HF (%)	Cellulose Acetate (%)
NaCl	92	95	97
$MgSO_4$	>99	>99	>99
Ethanol	25	30	9
Isopropanol	70	75	45
N-methyl-pyrrolidinone	86	84	60
Sucrose	>99	>99	>99

Test pressure: 1MPa for NTR membranes, 3 MPa for cellulose acetate.

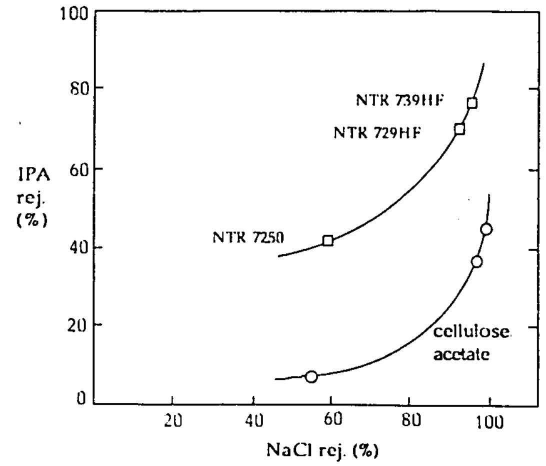


Fig. 16. Plot of isopropanol rejection versus NaCl rejection showing the relationship of the NTR-729 and NTR-739 membranes to the NTR-7250 membrane and to cellulose acetate [210].

membranes relative to the NTR-7250 membrane in a plot of isopropanol rejection versus NaCl rejection, along with comparative data for cellulose acetate. The primary advantage of these composite membranes is their tolerance to chlorinated water. The NTR-729HF was estimated to have a chlorine tolerance of approximately 20,000 ppm-hr; The NTR-739HF, approximately 10,000 ppm-hr.

Water softening membranes: the NF-50 membrane

In 1977, the idea of softening groundwaters by means of reverse osmosis with "loose" cellulose acetate asymmetric membranes was applied to Florida municipal well waters with good results [216]. This process became increasingly attractive when regulations on maximum concentration level (MCL) allowable for trihalomethane (THM) content in drinking water were established [216,217]. In Florida, as in many parts of the world, the water supply to a municipal tapwater system is contaminated with humic acids, which generate THMs upon chlorination. THMs themselves are not effectively removed by most reverse osmosis membranes. Glater and his co-workers [218] showed that chloroform, bromoform and carbon tetrachloride, at 50 mg/l, were all poorly rejected by cellulose acetate, asymmetric polyamide, and composite polyamide (A-15) membranes. Wilson et al. [219] further reported that reverse osmosis rejection of THMs declines during the first few days of operating time for a thin film composite membrane, even while rejection of total dissolved solids (TDS) remains stable. This is illustrated in Fig. 17. Similar results have been observed by Sorg and Love [220] in studies at a U.S. Environmental Protection Agency laboratory. Lynch and Smith [221] have found during studies on the reverse osmosis concentration of trace organics in drinking water, using cellulose acetate and FT-30 membranes, that up to 70% of low molecular weight organics (e.g. chloroform) were lost, as determined by mass balance determinations.

It would appear that the composite membranes in particular behave somewhat like chromatographic media, initially absorbing a large portion of the THMs that permeate through the barrier layer, later on eluting the absorbed THMs or simply reaching an absorption isotherm.

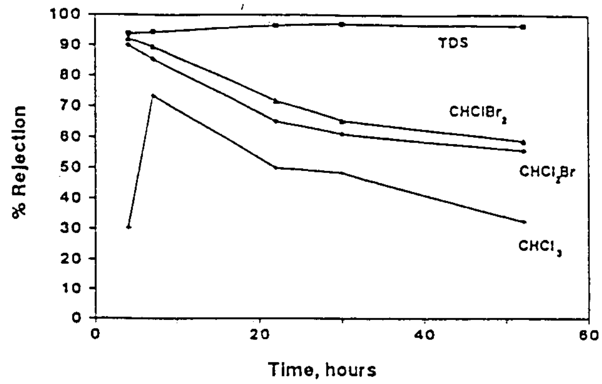


Fig. 17. Graph of solute rejection versus time showing the decline in rejection of a composite membrane toward chloroform and other low molecular weight volatile organic solutes [219].

Compared to THM removal by reverse osmosis, removal of humic acids from a municipal water source by water softening membranes would be an attractive alternative. FilmTec introduced two new composite membranes in 1985, the NF-50 and NF-70 membranes, which showed great promise for water softening and for simultaneous removal of THM-forming potential. Performance characteristics of these membranes compared to NF-40 have been listed by Eriksson [85], along with discussion of applications and field data. These performance characteristics are shown in Table 12.

The NF-50 and NF-70 membranes are both composite membranes in which the barrier layer is a fully aromatic crosslinked polyamide. Both are mildly anionic membranes, evidenced in part by their high $MgSO_4$ rejection compared to NaCl rejection. Their pH and temperature limits are generally similar to those of the FilmTec TW-30 and BW-30 membranes. The NF-50 membrane has since been discontinued because it tended to tighten during operation, becoming indistinguishable from NF-70 in long term field performance.

The potential of low pressure membranes has been evaluated by Taylor et al. [222]. Seven membranes, including reverse osmosis, nanofiltration and ultrafiltration types, were tested for effectiveness in removing THM precursors. These membranes and their performance results in a field test at a location identified as ACME Improvement District are shown in Table 13. Only the first two membranes on this list provided the desired degree of removal of THM forming potential (THMFP).

TABLE 12

Operating conditions and performance data for FilmTec NF membranes

	NF-50	NF-70	NF40
Pressure to produce 43 l/m^2-hr flux (bar)	4	6	20
Operating pH range	2-10	3-9	2-10
Max. temp. (°C)	45	45	45
Approx. solute rej. (%)			
NaCl	50	70	45
$MgSO_4$	90	98	95
Glucose	90	98	90
Sucrose	98	99	98

Taylor concluded from this study that the NF-50/NF-70 water softening membrane was as productive in terms of water throughput as any of those tested, and held THMs to less than the maximum allowed concentration (through removal of THMFP) while simultaneously reducing total hardness (TH) by 70%.

Taylor and co-workers [223] then used the NF-70 membrane in a one year pilot test encompassing 4000 hr of operation time at Flagler Beach, FL, running at a system inlet pressure of 141 psig, a system average flux of 12.9 gfd, and a system recovery of 78%. Table 14 summarizes operating data for this plant. Other data on the NF-70 membrane for water softening have been published by Conlan and McClellan [216] and others [85,86,91].

Another possible application of this water softening membrane is the reduction of naturally occurring radium content in some well waters, for drinking water purposes [85]. Many communities in Illinois, Wisconsin and Iowa have naturally occurring radium in their aquifers. Radium concentration in the nanofiltration concentrate stream, even at 75 to 85% system recoveries, is low enough for surface stream disposal, while permeate levels meet potable water standards.

The actual composition of the NF-50 and NF-70 membranes has not been disclosed other than their being aromatic polyamides. Examination of FilmTec patent literature showed a patent by Cadotte and Walker [224], in which a membrane having an interfacially formed, crosslinked, aromatic polyamide barrier layer was treated with a combination of hot phos-

TABLE 13

Percentage removal of THMFP, color and total hardness from groundwater by various membrane types

Source	Membrane	Type	MWCO	Removal (%)		
				THMFP	Color	TH
FilmTec	BW-30	RO	100	97	97	96
FilmTec	NF-50 (NF-70)	NF	400	96	97	70
DSI[a]	G-10	UF	2,000	56	60	13
DSI[a]	G-50	UF	20,000	37	37	7
FilmTec	UFP-4040	UF	20,000	19	9	0
Osmonics	PT-2	UF	20,000	3	6	1
Osmonics	PT-4	UF	40,000	2	9	0

[a] DSI = Desalination Systems, Inc.

TABLE 14

Summary of NF-70 system rejection data at Flagler Beach, Florida

Parameter	Feed (mg/l)	Reject (mg/l)	Permeate (mg/l)	Rejection (%)
pH	5.8	6.2	5.4	-
TDS	640	2,266	110	84
Alk as $CaCO_3$	175	556	36	74
TH as $CaCO_3$	359	1,407	34	91
CaH as $CaCO_3$	346	1,326	30	91
Na	51	124	22	57
Cl	103	317	27	74
DOC	11	39	2	86
TOXFP	1.02	4.11	0.0334	97
THMFP	0.40	2.01	0.0200	95
Iron	0.16	0.86	0.0450	68
SO_4	206	883	5	97
Color (cpu)	29	108	2	94

TH = total hardness; CaH = calcium hardness; DOC = dissolved organic carbon; TOXFP = total organic halide forming potential; THMFP = trihalomethane forming potential.

phoric acid and tannic acid. This produced a modified membrane having a greatly increased water flux and reduced salt rejection. The NF-50 and NF-70 membranes may possibly correspond to this patented membrane preparation procedure.

The available selection of potential water softening membranes broadened rapidly after these initial studies, as municipalities began to widely adapt membrane softening technology. In 1989, Conlon and McClellan [216] listed nine different membranes applicable for water softening, including UOP Fluid Systems modules 8231-LP (cellulose acetate blend) and 8921-UP (TFCS polyamide), FilmTec NF-70 and NF-40, Toray modules SCL-100 (modified cellulose acetate) and SU-600 (composite polyamide), Nitto Denko NTR-729HF, Desalination Systems Desal-5, and DuPont SM15 (high flux A-15 membrane).

Dynamic membranes

Kraus and co-workers [225] at Oak Ridge National Laboratory reported that salt-rejecting layers could be deposited on porous substrates by circulating low concentrations of polymeric polyelectrolytes over the substrates under pressure. For example, poly(vinyl benzyl trimethyl ammonium chloride) having a weight average molecular weight of approximately 140,000 was circulated in contact with an 0.2μ silver frit at a feed concentration of 250 ppm. The dynamically coated frit provided salt rejections for NaCl solutions that varied from 25% (0.1 *M* NaCl) to 85% (0.001 *M* NaCl). The